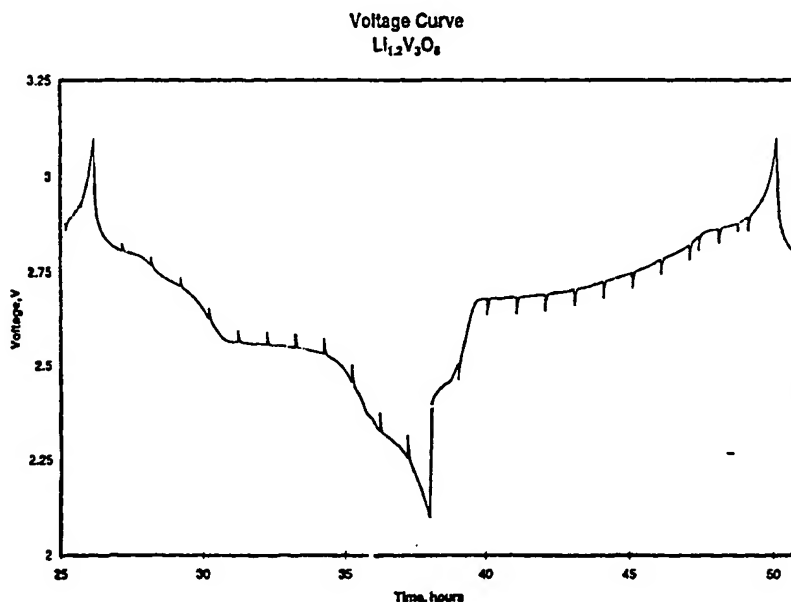




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01M 4/48	A1	(11) International Publication Number: WO 99/30378 (43) International Publication Date: 17 June 1999 (17.06.99)
<p>(21) International Application Number: PCT/US98/25613</p> <p>(22) International Filing Date: 3 December 1998 (03.12.98)</p> <p>(30) Priority Data: 08/985,441 5 December 1997 (05.12.97) US</p> <p>(71) Applicant: THE UNIVERSITY OF CHICAGO as operator of ARGONNE NATIONAL LABORATORY UNDER ITS U.S. DEPARTMENT OF ENERGY CONTRACT NO. W-31-109-ENG-38 [US/US]; 9700 South Cass Avenue, Argonne, IL 60439 (US).</p> <p>(72) Inventors: THACKERAY, Michael, M.; 1763 Cliffside Court, Naperville, IL 60565 (US). KAHAIAN, Arthur, J.; Apartment #2, 2027 West Cortland Street, Chicago, IL 60647 (US). VISSER, Donald, R.; 611 Clover Court, Naperville, IL 60540 (US). DEES, Dennis, W.; 6224 Middaugh Avenue, Downers Grove, IL 60516 (US). BENEDEK, Roy; 5727 Woodland Drive, Western Springs, IL 60558 (US).</p> <p>(74) Agent: MUETING, Ann, M.; Mueeting, Raasch & Gebhardt, P.A., P.O. Box 581415, Minneapolis, MN 55458-1415 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	

(54) Title: MODIFIED LITHIUM VANADIUM OXIDE ELECTRODE MATERIALS; PRODUCTS AND METHODS



(57) Abstract

A method of improving certain vanadium oxide formulations is presented. The method concerns fluorine doping formulations having a nominal formula of LiV_3O_8 . Preferred average formulations are provided wherein the average oxidation state of the vanadium is at least 4.6. Herein preferred fluorine doped vanadium oxide materials, electrodes using such materials, and batteries including at least one electrode therein comprising such materials are provided.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

MODIFIED LITHIUM VANADIUM OXIDE ELECTRODE MATERIALS; PRODUCTS AND METHODS

Field of the Invention

The present invention relates to certain modified lithium vanadium oxides.

5 Included are preferred oxides according to the general formula $\text{Li}_{1.2}\text{V}_3\text{O}_{8.5}\text{F}_8$ and certain related oxides such as $\text{Li}_{1.2}\text{V}_{3-x}\text{M}_x\text{O}_{8.5}\text{F}_8$, wherein M can be a variety of cations (or a mixture of cations). The invention concerns the utilization of such oxide materials as electrode materials, for example, as cathode materials in lithium batteries. The disclosure concerns preferred formulations of such materials, preferred methods for preparation of
10 them, products including such materials and methods of use.

Background of the Invention

The negative electrode (anode) of a high density lithium battery typically comprises one or more of a variety of any suitable lithium-containing substances such as: metallic lithium; lithium-metal alloys; lithium metal oxides; or, lithium carbon
15 composites. The positive electrode (cathode) is typically a lithium vanadium oxide, of the nominal or base formula LiV_3O_8 . The electrodes may be coupled using a liquid electrolyte or a solid electrolyte such as a solid polymer electrolyte, or a combination of liquid and solid electrolytes. The electrolyte may specifically be a "plasticized"
20 electrolyte in which a liquid electrolyte component is contained within a polymer electrolyte.

During discharge, lithium ions are electrochemically inserted into the lithium vanadium oxide structure by a process that is commonly referred to as intercalation. A reverse process occurs during charge. The vanadium ions of the host electrode structure are reduced and oxidized during discharge and charge, respectively. Conversely, the
25 negative electrode is oxidized during discharge when lithium ions are released from the electrode into the electrolyte, and it is reduced during the reverse process on charge.

Lithium ions, therefore, shuttle between the two electrodes during the electrochemical discharge and charge processes.

It is advantageous for batteries, such as lithium batteries, to have a high electrochemical "capacity" or energy storage capability. In lithium batteries, this can be achieved if the positive and negative electrodes can accommodate a significant amount of lithium. Furthermore, in order to have a good cycle life, the positive and negative electrodes should have the ability to accommodate and release lithium in a reversible manner, i.e., without significant "capacity fade". Thus, the structural integrity of the electrodes should be maintained during lithium insertion/extraction for numerous cycles.

10 Summary of the Invention

According to the present invention, a vanadium oxide material doped with fluorine is provided. Preferred formulations, providing for an overall charge balance in which the average, calculated, oxidation state of vanadium is at least 4.6, usually at least 4.8 and preferably at least 4.9, are provided.

15 The invention also concerns the provision of electrodes including lithium vanadium oxide according to the preferred general formula; and, batteries including an electrode as characterized. The invention further concerns a method of modifying a nominal vanadium oxide formula through fluorine doping.

Brief Description of the Drawings

20 Figure 1 is a discharge/charge profile of an electrochemical cell having, as an electrode, $\text{Li}_{1.2}\text{V}_3\text{O}_8$.

Figure 2 is an individual plot of discharge capacity versus the cycle number for a battery having as an electrode, $\text{Li}_{1.2}\text{V}_3\text{O}_8$.

Figure 3 is a plot of discharge capacity v. cycle number for a fluorine-doped electrode, specifically $\text{Li}_{1.2}\text{V}_3\text{O}_{7.9}\text{F}_{0.1}$.

25

Figure 4 is a plot of discharge capacity v. cycle number for a fluorine-doped electrode, specifically $\text{Li}_{1.2}\text{V}_3\text{O}_{7.8}\text{F}_{0.2}$.

Figure 5 is a plot of discharge capacity v. cycle number for a fluorine-doped electrode, specifically $\text{Li}_{1.25}\text{V}_{2.95}\text{O}_{7.8}\text{F}_{0.2}$.

5 Figure 6 is a plot of discharge capacity v. cycle number for a fluorine-doped electrode, specifically $\text{Li}_{1.2}\text{V}_{2.8925}\text{Ti}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$.

Figure 7 is a plot of discharge capacity v. cycle number for a fluorine-doped electrode, specifically $\text{Li}_{1.2}\text{V}_{2.8925}\text{Zr}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$.

10 Figure 8 is a plot of discharge capacity v. cycle number for a fluorine-doped electrode, specifically $\text{Li}_{1.2}\text{V}_{2.8}\text{Ti}_{0.1}\text{Mo}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$.

Figure 9 is an X-ray pattern for $\text{Li}_{1.2}\text{V}_3\text{O}_8$.

Figure 10 is an X-ray diffraction pattern for $\text{Li}_{1.2}\text{V}_3\text{O}_{7.9}\text{F}_{0.1}$.

Figure 11 is an X-ray diffraction pattern for $\text{Li}_{1.2}\text{V}_3\text{O}_{7.8}\text{F}_{0.2}$.

Figure 12 is an X-ray diffraction pattern for $\text{Li}_{1.25}\text{V}_{2.95}\text{O}_{7.8}\text{F}_{0.2}$.

15 Figure 13 is an X-ray diffraction pattern for $\text{Li}_{1.2}\text{V}_{2.8925}\text{Ti}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$.

Figure 14 is an X-ray diffraction pattern for $\text{Li}_{1.2}\text{V}_{2.8925}\text{Zr}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$.

Figure 15 is an X-ray diffraction pattern for $\text{Li}_{1.2}\text{V}_{2.8}\text{Ti}_{0.1}\text{Mo}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$.

Figure 16 is a representation of the structure of $\text{Li}_{1.2}\text{V}_3\text{O}_8$.

Figure 17 is a structural representation of a discharged electrode product $\text{Li}_4\text{V}_3\text{O}_8$.

20 Figure 18 is a cross-sectional representation of a cell incorporating an electrode according to the present invention.

Figure 19 is a second schematic illustration of a cell.

Detailed Description

I. A General Description of LiV_3O_8 Electrode Materials

25 A preferred vanadium oxide electrode material, for use with respect to lithium batteries of concern to the present invention will be referenced generally as having a

"nominal" formula of $\text{Li}_x\text{V}_3\text{O}_8$, wherein x is typically at least 1.0, usually about 1.0-1.5 and often about 1.2. The crystalline structure of this material is relatively stable, and is preferential with respect to intercalation. This nominal or base formula is the approximate formula at complete charge.

5 Oxides of nominal formula $\text{Li}_x\text{V}_3\text{O}_8$ exhibit a distinctive X-ray diffraction pattern (XRD) and crystalline structure, as discussed below.

 The specific preferred stoichiometry for the most stable electrode in the charged state is $\text{Li}_{1.2}\text{V}_3\text{O}_8$. By this it is meant that the preferred material is formulated from precursor materials such that in a fully charged cell the average formulation of the
10 cathode, with respect to the vanadium oxide component, is $\text{Li}_{1.2}\text{V}_3\text{O}_8$. The average (calculated) vanadium valence in $\text{Li}_{1.2}\text{V}_3\text{O}_8$ is 4.933 or "nominally" 5.

 As the battery is discharged, lithium cations are inserted into the crystalline $\text{Li}_{1.2}\text{V}_3\text{O}_8$ electrode structure. This reduces the average oxidation state of the vanadium ions from 4.933 in $\text{Li}_{1.2}\text{V}_3\text{O}_8$ to 4.0 in $\text{Li}_4\text{V}_3\text{O}_8$, which represents the approximate
15 composition of the positive electrode in a discharged cell.

 According to the present invention, the nominal LiV_3O_8 structure, typically and preferably $\text{Li}_{1.2}\text{V}_3\text{O}_8$, is modified to advantage. The modification, in part, concerns "doping" with fluorine. The substitution of fluorine ions for some oxygen ions can lead to stabilization, as discussed below. In some instances, the "fluorine doping" is
20 accompanied by a preferred introduction of further cations, for example, additional lithium cations or other cations, into the crystalline structure.

II. Preferred Modified Electrode Materials

A. Electrode Materials in Which the Only Cations (other than impurities) Are Lithium and Vanadium

25 According to this aspect of the present invention, preparation of a lithium vanadium oxide of the general (base or nominal) formula $\text{Li}_x\text{V}_3\text{O}_8$ preferably wherein $x \geq 1$ (typically 1.0 to 1.5 and more preferably is about 1.2) is modified by fluorine substitution (doping) to lead to a preferred fluorine-doped material. For example, in a

particular embodiment, the oxygen ions may be partially substituted by fluorine, preferably to a material having the general formula $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}\text{F}_\delta$ wherein $0 < \delta \leq 1.0$. Typically and preferably, δ is within the range of 0.05 to 0.3.

In $\text{Li}_{1.2}\text{V}_3\text{O}_8$ the mean oxidation state of vanadium is 4.933. Substitution of
 5 fluorine for oxygen as characterized in the previous paragraph, but in such a manner that the vanadium oxide state is kept equal to or close to its relatively high original value of 4.933, more generally at least 4.6 (usually at least 4.8, typically and preferably at least 4.9), can be achieved by substituting some lithium ions for some of the vanadium ions. A class of stabilized lithium vanadium oxides (base formulation) according to this aspect of
 10 the invention would preferably be characterized by the following general formula: $\text{Li}_{1.2+\delta'}\text{V}_{3-\delta'}\text{O}_{8-\delta}\text{F}_\delta$ wherein δ' is equal to 0.254δ . The value for δ' results from a calculation as follows:

The charge balance must be zero, so:

Assuming a "preferred" average oxidation state for V ions of 4.933 in a
 15 fully-charged electrode, then:

$$(1)(1.2+\delta') + (4.933)(3-\delta') + (-2)(8-\delta) + (-1)(\delta) = 0$$

$$\text{or } 1.2 + \delta' + 14.799 \text{ (or about 14.8)} - 4.933\delta' - 16 + 2\delta - \delta = 0$$

$$\text{or } -3.933\delta' + \delta = 0$$

$$\text{so } \delta = +3.933\delta'$$

$$20 \quad \text{or } \delta' = 0.254\delta$$

Thus, for example, for $\delta=0.2$, the formula would be: $\text{Li}_{1.25}\text{V}_{2.95}\text{O}_{7.8}\text{F}_{0.2}$.

The type of calculation discussed above is sometimes referred to herein as a "valence type" calculation and can be applied to determine a variety of unknowns.

25 B. Electrode Materials In Which Cations Other Than Lithium And Vanadium Are Also Provided

In further embodiments of the present invention, in addition to substitution of fluorine for some oxygen compounds, substitution of vanadium by another element, preferably a cation in addition to lithium, is used. This can also be a method of

maintaining the average, calculated, oxidation state of vanadium at or near 4.933, or more generally at a value of at least 4.6 (usually at least 4.8, typically and preferably at least 4.9) in the fully charged state.

Substitution of a metal cation for some of the vanadium in the material results in a
 5 general formula as follows: $\text{Li}_{1.2}\text{V}_{3-\delta}\text{M}_{\delta}\text{O}_{8-\delta}\text{F}_{\delta}$ wherein the relationship between δ and δ' can be calculated in a like manner as given above, with an additional term corresponding to the valency of the cation M. For example, if the cation M is chosen to be a tetravalent cation such as titanium (Ti^{+4}) or zirconium (Zr^{+4}), the relationship between δ and δ' (calculated analogously to the calculation given above) is: $\delta' = 1.075\delta$

10 A base formula for a preferred group of such stabilized compounds would be as follows: $\text{Li}_{1.2}\text{V}_{3-\delta}\text{M}_{\delta}\text{O}_{8-\delta}\text{F}_{\delta}$ wherein M is a cation selected from Al, Si, P, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, La and mixtures thereof. Preferred cations, M, are those that form strong M-O bonds, such as Al, Si, P, Sc, Ti, Ge, Y, Zr, Nb, Mo and La. As an example, and using the valence calculation discussed above; for $\delta = 0.1$ and
 15 $\text{M}=\text{Ti}$, a preferred formula would be $\text{Li}_{1.2}\text{V}_{2.8925}\text{Ti}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$.

In general, it is preferred to use a transition element "M" (or mixture of elements of "M") which does not, in the amounts used, generate a significant amount of a second impurity phase along with $\text{Li}_{1.2}\text{V}_3\text{O}_8$.

In various embodiments of the present invention, it is possible to use two or more
 20 different cations as substituents for some of the vanadium ions. For example, it is possible to replace two pentavalent vanadium ions (V^{+5}) in the lithium-vanadium-oxide crystal lattice by one hexavalent molybdenum (Mo^{+6}) ion and one tetravalent zirconium (Zr^{+4}) or titanium (Ti^{+4}) ion. In this instance, substitution of two metal cations for some of the vanadium in the material results in the general formula: $\text{Li}_{1.2}\text{V}_{3-2\delta}\text{M}'_{\delta}\text{M}''_{\delta}\text{O}_{8-\delta}\text{F}_{\delta}$
 25 wherein the relationship between δ and δ' can be calculated in a like manner as given above.

Thus, as an example, for $M' = \text{Mo}^{+6}$, $M'' = \text{Ti}^{+4}$, $\delta = 0.1$ and $\delta' = 0.1$, a preferred formula would be: $\text{Li}_{1.2}\text{V}_{2.8}\text{Mo}_{0.1}\text{Ti}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$.

III. Methods of Preparation

Materials according to the present invention can be readily prepared by
5 modifications to known techniques for manufacture of $\text{Li}_x\text{V}_3\text{O}_8$.

For example, $\text{Li}_{1.2}\text{V}_3\text{O}_8$ electrode materials can be manufactured by reaction of LiOH with NH_4VO_3 in methanol, with follow up firing to 400°C ; as described further in the experimental section.

Fluorine introduction can be readily achieved by introducing LiF in place of some
10 of the lithium hydroxide, in an appropriate amount to achieve the desired stoichiometry. Additional modifications in lithium can be introduced by adding further LiOH .

Similarly, other metal cations can be introduced into the crystal structure of the electrode. For example, titanium can be introduced by the addition of $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ to the reaction mixture, zirconium by $\text{Zr}[\text{OCH}(\text{CH}_3)_2]_4$, $(\text{CH}_3)_2\text{CH}_2\text{OH}$ and molybdenum by
15 MoO_3 . For other cations, the compounds can be selected from oxides, hydroxides or salts such as alkoxides, oxalates, acetates and nitrates.

Electrodes can be prepared from the oxide base by coating onto a metallic current collector a slurry containing the oxide base, a polymeric binder such as polyvinylidene fluoride (PVDF), an electrically conductive particle such as conductive
20 carbon particles, and a solvent such as toluene, and drying the coating, to form the electrode.

IV. Some Theories For Certain Observed Stabilization Effects

Electrode materials of the type described herein would typically be used in high energy density lithium storage batteries. The capacity fade that occurs with time for
25 certain types of such batteries during repeated discharge and charge can be attributed to a number of possible factors. $\text{Li}_{1.2}\text{V}_3\text{O}_8$ has a layered-type crystal structure. During

discharge, lithium ions are inserted into a $\text{Li}_{1.2+x}\text{V}_3\text{O}_8$ structure (typically $0 \leq x' \leq 2.8$). Capacity fade phenomena could result for example, either from (1) structural fatigue due to anisotropic variations in the lattice parameters during charge and discharge, or (2) migration of vanadium ions from their original positions into the layers occupied by
5 lithium, thereby, restricting lithium mobility, or (3) the dissolution of some vanadium from the crystal lattice into the electrolyte, or a combination of (1), (2) and (3).

In preferred lithium vanadium oxide cathode arrangements according to the present invention, at the "top of the charge", the vanadium is in an average oxidation state approaching V^{+5} (typically and preferably about 4.933, more generally at least 4.6) and at
10 the end of discharge it is closer to V^{+4} . Vanadium in lower oxidation states is believed to be somewhat more soluble in certain electrolytes than at higher oxidation states. This could be partly responsible for some of the observed deterioration of the cathode operation, with cycling for certain types of batteries.

Without being bound to any particular theory, it is presently believed that the
15 fluorine-doped systems (in particular the fluorine-doped and M-cation doped systems) are stabilized by introduction of the fluorine ions and M cations into the crystal structure. A possible reason for this could be differences in strength between vanadium-fluorine, vanadium-oxygen, and M-oxygen bonds. It can be reasoned that the minor introduction of fluorine ions and, if desired M cations, may add integrity to the vanadium oxide
20 crystalline structure, as a result of the introduction of strong vanadium-fluorine and M-oxygen bonds. The net result of this could be either or both of inhibiting vanadium migration and/or inhibiting solubility. In some instances this may manifest itself by a lessening of capacity fade.

In general, the preferred formulations provided are arrived at by focusing on two
25 principal factors:

1. A desire to maintain the vanadium valence state, at the top of charge, as close to 4.933 as reasonably possible, and more generally at least 4.6 (usually at least 4.8 and preferably at least 4.9) in the stabilized $\text{Li}_{1.2}\text{V}_3\text{O}_8$ (base) crystal structure.

2. Introduction of no more fluorine ions into the crystalline structure than is
5 useful to achieve the desired level of stabilization, because of a desire not to greatly depart from the stoichiometry of the $\text{Li}_{1.2}\text{V}_3\text{O}_8$ base, and to keep the level of fluorine (a chemically aggressive reagent) in the oxide as low as reasonably possible.

In general, the crystalline structure of $\text{Li}_{1.2}\text{V}_3\text{O}_8$ is layered. Three vanadium ions and one lithium ion typically occupy octahedral sites in the $\text{Li}_{1.2}\text{V}_3\text{O}_8$ structure; the
10 remaining (for example 0.2) lithium ions occupy tetrahedral sites. During discharge, the lithium ions migrate into neighboring octahedral sites to generate a stable defect rocksalt structure. The approximate composition at the end of discharge is $\text{Li}_4\text{V}_3\text{O}_8$.

Substitution of oxygen with fluorine in $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}\text{F}_\delta$ results in a lowering of the average oxidation state of the vanadium ions in the structure. Compensation for this can
15 be accomplished by increasing the presence of other cations, for example, by introduction of more lithium or by introduction of other cations. As a result, a charge balance, with the average vanadium charge of about 4.933 (generally at least 4.6, usually at least 4.8 and preferably at least 4.9), calculated as discussed above, can be maintained.

Preferred cations to introduce for this purpose are titanium and/or zirconium,
20 although other cations and even mixtures, can be used. The titanium or zirconium doped systems are advantageous because of the relatively strong titanium-oxygen or zirconium-oxygen bonds in the crystal structure. It can be reasoned that such bonds will serve to strengthen and maintain the integrity of the overall crystal structure, particularly during cell operation when lithium is being repeatedly inserted into and extracted from the
25 structure.

V. General Formulae of Preferred Materials Based on the Above-Recited Principles and Descriptions.

A general formula of a preferred vanadium oxide material, useable as a cathode material as described above at least when defined in the charged state, would be as follows:



wherein preferably:

- (a) $0 < \delta \leq 1$ (preferably $0.05 \leq \delta \leq 0.3$)
- (b) $0 \leq y \leq 0.5$
- (c) x is non-zero (typically and preferably $1 \leq x \leq 1.5$ usually x is about 1.2;
- 10 (d) x , y and z are selected such that the average, calculated, oxidation state of V is at least 4.6, more preferably at least 4.8 and most preferably at least 4.9; and,
- (e) M is selected from ions of Al, Si, P, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, La and mixtures thereof (preferably Ti, Y, Zr, Mo and mixtures thereof).

- 15 In one preferred embodiment: $y=0$; $z=3$; and, $x=1.2$. If lithium presence is increased to maintain a preferred calculated valance for the vanadium, in one preferred embodiment: $y=0$; $z=3-\delta'$; and $x=1.2 + \delta'$, wherein $\delta' = 0.254\delta$. In those formulations in which $y>0$, preferably: M is Ti or Zr; $x=1.2$; $z=3-\delta'$; and $y=\delta'$; wherein $\delta'=1.075\delta$.

Preferred electrodes comprise a vanadium oxide base according at least one of the
20 preferred formulae recited above; and, preferred battery constructions include at least one preferred electrode as characterized.

It should be appreciated that in some instances M may be a mixture of cations and thus M_y would comprise such formulae as: $M'_y M''_y$; $M'_y M''_y M'''_y$; ... etc. The term
25 " M_y " is intended to include mixtures of this type. In such instances the limitation on " y " is intended to be on the averaged cation " M " resulting from averaging the valence of the various M' , M'' , etc., using a mole-weighted, valence charge balance calculation analogous

to the ones discussed above. Preferred electrodes which contain a mixture of cations are those in which M is derived from Ti, Y, Zr and Mo.

As indicated above, the formulae given herein for the preferred vanadium oxide materials are generally in reference to the material as it would be found in an electrode in the fully charged state. During discharge, and intercalation, a lithium ion introduction will modify the formulae.

VI. An Example Battery Construction

Typically battery constructions that can use the preferred cathode materials according to the present invention include otherwise conventional coin cells, wound cells and stacked cells in which the cathode oxide is replaced with the preferred oxide(s) described herein. Various useable conventional constructions are described in Handbook of Batteries, 2d Ed., edited by D. Linden et al., McGraw-Hill, 1995, the disclosure of which is incorporated herein by reference.

An example cell is shown in Fig. 18. The cell may generally be according to the description of U.S. Patent 4,803,137, incorporated herein by reference, except in that the cathode includes a vanadium oxide material as described herein. Referring to Fig. 18, the cell depicted includes: a cathode 1; a positive electrode current collector 2; a positive electrode casing 3; an anode U; a negative electrode current collector 5; a negative electrode casing 6; separator/electrolyte 7; and, insulating polypropylene gasket 8. With a vanadium oxide material as described herein, the cell would operate in the otherwise typical fashion.

Another schematic illustration of the electrochemical cell is shown in Fig. 19. The cell is designated 15, and the anode (negative electrode), electrolyte and cathode (positive electrode) are designated 11, 12, and 13, respectively, with the anode 11 separated from the cathode 12 by the electrolyte 12. Suitable terminals designated 14 are provided in electronic contact with the 11 anode and the 13 cathode. The cell 15 is contained in a housing, designated 16, which insulates the anode from the cathode. The

cell 15 may include, at the cathode 13, vanadium oxide material according to the present invention.

VII. Experimental

5 A. Preparation of Various Oxide Materials for Testing

Example 1. $\text{Li}_{1.2}\text{V}_3\text{O}_8$ (A comparative example)

For this preparation, 1.2 moles of $\text{LiOH}\cdot\text{H}_2\text{O}$ and 3 moles of NH_4VO_3 were suspended in methanol and milled for 48 hours. The methanol was evaporated and the dry solid precursor heated in air. The sample was heated to 400°C at a rate of $1^\circ\text{C}/\text{min}$. and held at 400°C for 24 hours. It was then allowed to cool to room temperature (at about a $1^\circ\text{C}/\text{min}$. cooling rate). The product was ground to a fine powder by mortar and pestle and submitted for phase identification by X-ray powder diffraction.

Example 2. $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}\text{F}_\delta$

For these preparations, $1.2-\delta$ moles of $\text{LiOH}\cdot\text{H}_2\text{O}$, δ moles of LiF and 3 moles of NH_4VO_3 were suspended in methanol and milled for 48 hours. The methanol was evaporated and the dry solid precursor, slightly yellow in color when compared to $\text{Li}_{1.2}\text{V}_3\text{O}_8$, was heated in air. The sample was heated to 400°C at a rate of $1^\circ\text{C}/\text{min}$. and held at 400°C for 24 hours, then allowed to cool to room temperature (at about a $1^\circ\text{C}/\text{min}$. cooling rate). The product was ground to a fine powder and submitted for phase identification by X-ray powder diffraction.

Example 3. $\text{Li}_{1.25}\text{V}_{2.95}\text{O}_{7.8}\text{F}_{0.2}$ [i.e., $\text{Li}_{1.2+\delta'}\text{V}_{3-\delta'}\text{O}_{8-\delta'}\text{F}_{\delta'}$, wherein $\delta' = 0.2545\delta$ for $\delta = 0.2$].

For this preparation, 1.05 moles of $\text{LiOH}\cdot\text{H}_2\text{O}$, 0.2 moles of LiF and 2.95 moles NH_4VO_3 were suspended in methanol and milled for 48 hours. The methanol was evaporated and the dry solid precursor heat treated in air. The sample was heated to 400°C at a rate of $1^\circ\text{C}/\text{min}$. and held at 400°C for 24 hours, then allowed to cool to room temperature (at about a $1^\circ\text{C}/\text{min}$. cooling rate). The product was ground to a fine powder and submitted for phase identification by X-ray powder diffraction.

Example 4. $\text{Li}_{1.2}\text{V}_{2.8925}\text{Ti}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$

For this preparation, 1.1 moles of $\text{LiOH}\cdot\text{H}_2\text{O}$, 0.1 moles of LiF , 0.1075 moles of $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, and 2.8925 moles of NH_4VO_3 were suspended in methanol and milled for 48 hours. The methanol was evaporated and the dry solid precursor heat treated in air.
5 The sample was heated to 400°C at a rate of $1^\circ\text{C}/\text{min.}$ and held at 400°C for 24 hours, then allowed to cool to room temperature (at about a $1^\circ\text{C}/\text{min.}$ cooling rate). The product was ground to a fine powder and submitted for phase identification by X-ray powder diffraction.

Example 5. $\text{Li}_{1.2}\text{V}_{2.8925}\text{Zr}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$

10 For this preparation, 1.1 moles of $\text{LiOH}\cdot\text{H}_2\text{O}$, 0.1 moles of LiF , 0.1075 moles of $\text{Zr}[\text{OCH}(\text{CH}_3)_2]_4(\text{CH}_3)_2\text{CH}_2\text{OH}$ and 2.8925 moles of NH_4VO_3 were suspended in methanol and milled for 48 hours. The methanol was evaporated and the dry solid precursor was heat treated in air. The sample was heated to 400°C at a rate of $1^\circ\text{C}/\text{min.}$ and held at 400°C for 24 hours, then allowed to cool to room temperature (at about a
15 $1^\circ\text{C}/\text{min.}$ cooling rate). The product was ground to a fine powder and submitted for phase identification by X-ray powder diffraction.

Example 6. $\text{Li}_{1.2}\text{V}_{2.8}\text{Ti}_{0.1}\text{Mo}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$

1.1 moles of $\text{LiOH}\cdot\text{H}_2\text{O}$, 0.1 moles of LiF , 0.1 moles of $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, 0.1 moles of MoO_3 and 2.8 moles of NH_4VO_3 were suspended in methanol and milled for 48
20 hours. The methanol was evaporated and the dry solid precursor was heat treated in air. The sample was heated to 400°C at a rate of $1^\circ\text{C}/\text{min.}$ and held at 400°C for 24 hours, then allowed to cool to room temperature (at about a $1^\circ\text{C}/\text{min.}$ cooling rate). The product was ground to a fine powder and submitted for phase identification by X-ray powder diffraction.

B. Electrochemical Testing

Example 7. The materials of Examples 1-6 were screened for electrochemical performance in standard 1225 coin cells. A cathode laminate of each material was prepared by mixing, by weight: 81% active (test) material; 10% Kynar (binder available from ELF Autochem North America, Inc. of Philadelphia, PA); and, 9% carbon (VX C72 available from CABOT Corp. of Boston, MA), with milling in tetrahydrofuran. For $\text{Li}_{1.2}\text{V}_3\text{O}_8$, two separate cathode laminates were made and evaluated, to examine possible variance based on production variables.

To prepare the cathode, the laminate mixture was poured onto a smooth surface and applied with a doctor-blade to uniform thickness. When the mixture was sufficiently dry, a laminate disk approximately $\frac{1}{4}$ inch (6.35 mm) in diameter was punched out. The disks were dried in a vacuum overnight at about 80°C. The coin cells were then prepared by stacking, in order: can (hardware); copper spacer; lithium disk; separator; a few drops of dimethoxyethane (to help wet the separator); 1.0 M LiPF_6 in ethylene carbonate/dimethylcarbonate, 50%/50% by weight (electrolyte); cathode laminate; insulating spacer, to assure stack height of 75/80 mil.; and cap (hardware). The coin cells were crimped in a hydraulic press.

Coin cells of general notation, $\text{Li}/1.0\text{M LiPF}_6$, DMC, EC/ $\text{Li}_{1.2}\text{V}_3\text{O}_8$ (or doped) material were cycled at constant current (typically 0.1 mA) between 3.1-2.1 V for at least 20 cycles. The test equipment was a Series 2000 Maccor Cycler.

C. Evaluation of Data

A typical discharge/charge profile of a $\text{Li}/1.0\text{M LiPF}_6$, DMC, EC/ $\text{Li}_{1.2}\text{V}_3\text{O}_8$ cell is shown in Figure 1. This figure is also representative of the typical voltage profiles of a cell containing the fluorine-doped electrodes. The principles of the invention were demonstrated in the electrochemical data obtained from standard (undoped) $\text{Li}_{1.2}\text{V}_3\text{O}_8$ electrodes and from various fluorinated electrodes. Individual plots of discharge capacity vs. cycle number are provided in Figures 2 to 8 for: (1) standard (base) $\text{Li}_{1.2}\text{V}_3\text{O}_8$,

(Example 1, Fig. 2); (2) $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}\text{F}_\delta$ with $\delta=0.1$ (Example 2, Fig. 3) and $\delta=0.2$ (Example 2, Fig. 4); (3) $\text{Li}_{1.2+\delta'}\text{V}_{3-\delta'}\text{O}_{8-\delta}\text{F}_\delta$ with $\delta'=0.05$ and $\delta=0.2$, i.e., $\text{Li}_{1.25}\text{V}_{2.95}\text{O}_{7.8}\text{F}_{0.2}$ (Example 3, Fig. 5); (4) $\text{Li}_{1.2}\text{V}_{2.8925}\text{Ti}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$ (Example 4, Fig. 6), $\text{Li}_{1.2}\text{V}_{2.8925}\text{Zr}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$ (Example 5, Fig. 7); and (5) $\text{Li}_{1.2}\text{V}_{2.8}\text{Ti}_{0.1}\text{Mo}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$ (Example 6, Fig. 8). It was observed that, in general, the fluoride-doped electrodes led to higher capacities compared to the standard (base) $\text{Li}_{1.2}\text{V}_3\text{O}_8$ material. The best electrode materials observed to date in the experiments, with respect to capacity fade, included the $\text{Li}_{1.2}\text{V}_{2.8925}\text{Ti}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$ and $\text{Li}_{1.2}\text{V}_{2.8}\text{Ti}_{0.1}\text{Mo}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$ samples. It is believed that further improvements in the performance of these fluorine-doped materials can be expected, once the composition and processing techniques and conditions are optimized.

Table 1 summarizes the typical electrochemical data that were obtained from fluorine-doped and M-doped LiV_3O_8 electrodes in accordance with this invention. The relative stability of the various electrodes is given as a function of capacity fade between cycle 2 and cycle 20, and compared with the performance of a standard electrode of nominal composition $\text{Li}_{1.2}\text{V}_3\text{O}_8$.

Table 1 demonstrates a general improvement in the electrochemical performance of the modified $\text{Li}_{1.2}\text{V}_3\text{O}_8$ electrodes in terms of both capacity and capacity fade after 20 cycles compared with the standard $\text{Li}_{1.2}\text{V}_3\text{O}_8$ electrode, and particularly those electrodes that doped with both fluorine and M cations. Table 1 demonstrates that a wide variety of dopant M cations can be used to improve the $\text{Li}_{1.2}\text{V}_3\text{O}_8$ electrode performance, particularly in terms of improving the capacity fade of the electrochemical cell.

TABLE 1

Material	Capacity	(mAh/g)	Capacity Fade (%)
	<u>Cycle 2</u>	<u>Cycle 20</u>	
$\text{Li}_{1.2}\text{V}_3\text{O}_8$	191	151	21
$\text{Li}_{1.2}\text{V}_3\text{O}_{7.9}\text{F}_{0.1}$	203	161	21
$\text{Li}_{1.2}\text{V}_3\text{O}_{7.8}\text{F}_{0.2}$	227	209	7
$\text{Li}_{1.25}\text{V}_{2.95}\text{O}_{7.8}\text{F}_{0.2}$	191	153	20
$\text{Li}_{1.2}\text{V}_{2.8925}\text{Ti}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$	232	208	10
$\text{Li}_{1.2}\text{V}_{2.8925}\text{Zr}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$	232	203	12
$\text{Li}_{1.2}\text{V}_{2.8}\text{Ti}_{0.1}\text{Mo}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$	237	229	3
$\text{Li}_{1.2}\text{V}_{2.85}\text{Ti}_{0.075}\text{Mo}_{0.075}\text{O}_{7.95}\text{F}_{0.05}$	245	210	14
$\text{Li}_{1.2}\text{V}_{2.8}\text{Zr}_{0.1}\text{Mo}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$	163	168	-3
$\text{Li}_{1.2}\text{V}_{2.85}\text{Fe}_{0.15}\text{O}_{7.9}\text{F}_{0.1}$	209	188	10
$\text{Li}_{1.2}\text{V}_{2.93}\text{Ni}_{0.07}\text{O}_{7.8}\text{F}_{0.2}$	219	180	18
$\text{Li}_{1.2}\text{V}_{2.8}\text{Ti}_{0.2}\text{O}_{0.9}\text{F}_{0.1}$	208	183	12

D. X-ray Diffraction Patterns

Powder X-ray patterns of the various samples (1) standard (base) $\text{Li}_{1.2}\text{V}_3\text{O}_8$ (Fig. 9); (2) $\text{Li}_{1.2}\text{V}_3\text{O}_{8-\delta}\text{F}_\delta$ with $\delta=0.1$ (Fig. 10) and $\delta=0.2$ (Fig. 11); (3) $\text{Li}_{1.2+\delta}\text{V}_{3-\delta}\text{O}_{8-\delta}\text{F}_\delta$ with $\delta'=0.05$ and $\delta=0.2$, i.e., $\text{Li}_{1.25}\text{V}_{2.95}\text{O}_{7.8}\text{F}_{0.2}$ (Fig. 12); (4) $\text{Li}_{1.2}\text{V}_{2.8925}\text{Ti}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$ (Fig. 13); (5) $\text{Li}_{1.2}\text{V}_{2.8925}\text{Zr}_{0.1075}\text{O}_{7.9}\text{F}_{0.1}$ (Fig. 14); and, (6) $\text{Li}_{1.2}\text{V}_{2.8}\text{Ti}_{0.1}\text{Mo}_{0.1}\text{O}_{7.9}\text{F}_{0.1}$ (Fig. 15) are provided in the Figures.

From the X-ray diffraction data it can be seen that most of the fluorinated samples are essentially single phase systems and can be indexed to the same structure as the parent $\text{Li}_{1.2}\text{V}_3\text{O}_8$ material.

E. Illustrations of Structures

Structural representations of $\text{Li}_{1.2}\text{V}_3\text{O}_8$ and $\text{Li}_4\text{V}_3\text{O}_8$ are shown in Figures 16 and 17.

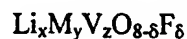
Referring first to Fig. 16, which represents the typical structure of LiV_3O_8 , and applies to the lithium vanadium oxide "base" materials according to the present invention, the gray spheres represent lithium cations which are located in octahedra and tetrahedra.

The vanadium layers are depicted as a combination of $[\text{VO}_6]$ octahedra and $[\text{VO}_5]$ square pyramids. The small open spheres on the polyhedra represent the oxygen ions. Figure 16 is also representative of the fluorine-doped systems, in which the fluorine ions partially substitute for some of the oxygen ions.

5 Figure 17 is a typical structural representation of a discharged electrode product $\text{Li}_4\text{V}_3\text{O}_8$. As before, the gray spheres represent lithium ions and the small open spheres the oxygen ions. In $\text{Li}_4\text{V}_3\text{O}_8$, the vanadium ions and lithium ions are all octahedrally coordinated. The vanadium layers, therefore, consist of only $[\text{VO}_6]$ octahedra. Figure 17 is also generally representative of the discharged fluorine-doped electrodes according to
10 the present invention.

What Is Claimed Is:

1. A vanadium oxide material according to the average formula:



5 wherein:

- (a) $0 < \delta \leq 1$;
(b) $0 \leq y \leq 0.5$;
(c) x is non-zero;
(d) x, y and z are selected such that the average, calculated, oxidation
10 state of V is at least 4.6; and
(e) M is selected from Al, Si, P, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn,
Ge, Y, Zr, Nb, Mo, La and mixtures thereof.

2. A vanadium oxide material according to claim 1, wherein:

- 15 (a) $y = 0$;
(b) $z = 3$; and
(c) $1 \leq x \leq 1.5$.

3. A vanadium oxide material according to claim 1, wherein:

- 20 (a) $y = 0$;
(b) $z = 3 - \delta'$; and
(c) $x = 1.2 + \delta'$
wherein $\delta' = 0.254\delta$

- 25 4. A vanadium oxide material according to claim 1, wherein:

- (a) the average oxidation state of V is at least 4.8.

5. A vanadium oxide material according to claim 1 wherein:
- (a) y is non-zero; and
 - (b) M is selected from Ti, Y, Zr, Mo and mixtures thereof.
- 5 6. A vanadium oxide material according to claim 1, wherein:
- (a) $x = 1.2$;
 - (b) $z = 3 - \delta'$;
 - (c) $y = \delta'$, wherein $\delta' = 1.075\delta$; and
 - (d) M is selected from Ti, Zr and mixtures thereof.
- 10 7. A vanadium oxide material according to claim 1 wherein:
- (a) $1 \leq x \leq 1.5$;
 - (b) $z = 2.8$;
 - (c) $\delta = 0.1$;
 - (d) y is non-zero; and
 - (e) M is selected from Ti, Y, Zr, Mo and mixtures thereof.
- 15 8. An electrode comprising:
- (a) a vanadium oxide base according to the average formula:
- 20
$$\text{Li}_x\text{M}_y\text{V}_z\text{O}_{8-\delta}\text{F}_\delta$$
- wherein:
- (i) $0 < \delta \leq 1$;
 - (ii) $0 \leq y \leq 0.5$;
 - (iii) x is non-zero;
 - (iv) x, y and z are selected such that the average oxidation state of V is
- 25 at least 4.6; and

(v) M is selected from Al, Si, P, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, La and mixtures thereof.

9. An electrode according to claim 8, wherein:

- 5
- (a) $y = 0$;
 - (b) $z = 3$; and
 - (c) $1 \leq x \leq 1.5$.

10. An electrode material according to claim 8, wherein:

- 10
- (a) $y = 0$;
 - (b) $z = 3 - \delta'$; and
 - (c) $x = 1.2 + \delta'$;
- wherein $\delta' = 0.254\delta$

15 11. An electrode according to claim 8, wherein:

- (a) the average oxidation state of V is at least 4.8.

12. An electrode according to claim 8, wherein:

- 20
- (a) y is non-zero; and
 - (b) M is selected from Ti, Y, Zr, Mo and mixtures thereof.

13. An electrode according to claim 8, wherein:

- 25
- (a) $x = 1.2$;
 - (b) $z = 3 - \delta'$;
 - (c) $y = \delta'$, wherein $\delta' = 1.0758$; and,
 - (d) M is selected from Ti, Zr and mixtures thereof.

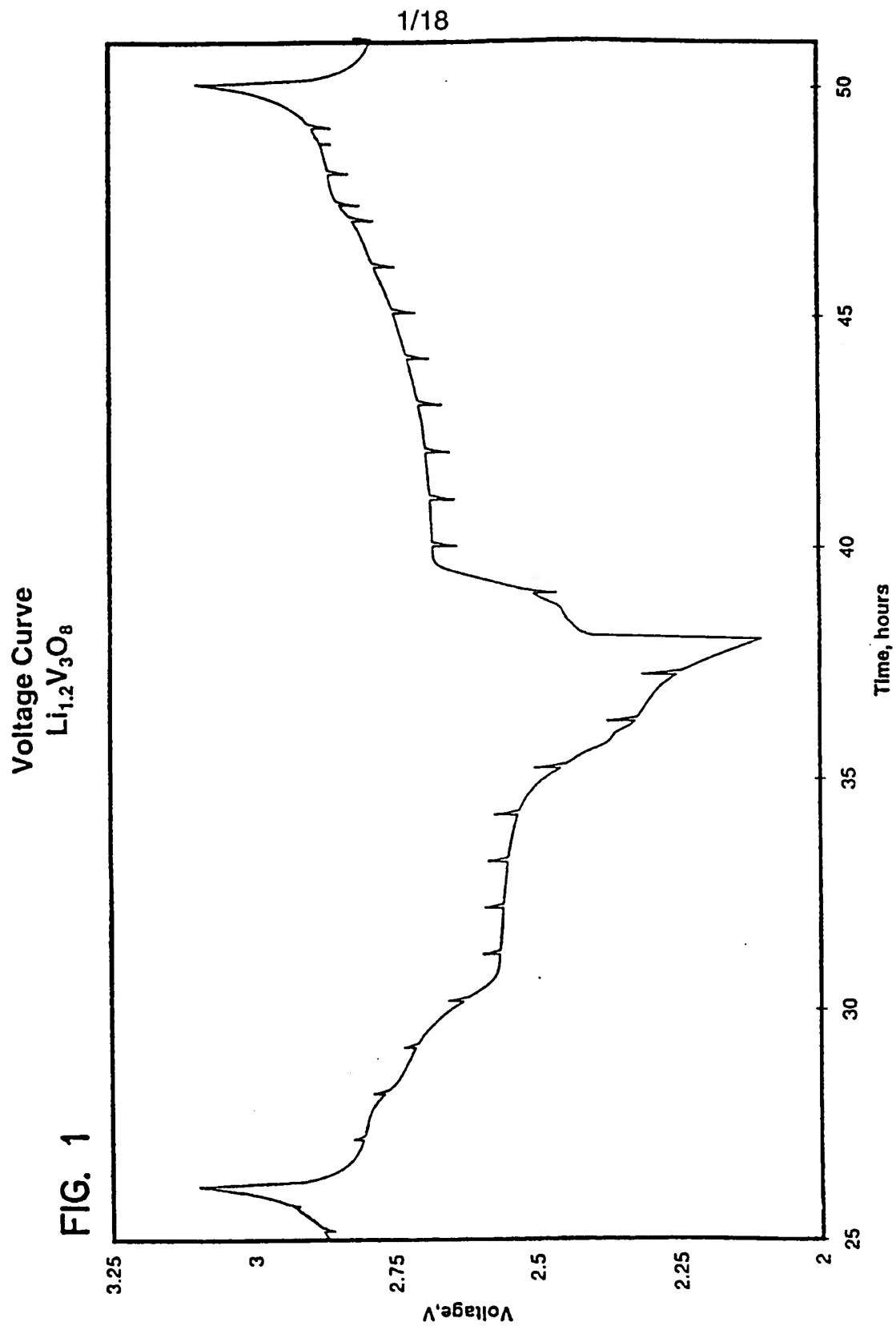
14. An electrode material according to claim 8, wherein:
- (a) $x = 1.2$;
 - (b) $z = 3 - \delta'$;
 - 5 (c) $y = \delta'$, wherein $\delta' = 1.075\delta$, and
 - (d) M is selected from Ti, Zr and mixtures thereof.
15. An electrode according to claim 8 further comprising:
- (a) binder; and
 - 10 (b) conductive material.
16. An electrochemical cell comprising:
- (a) a cathode comprising a vanadium oxide base according to the average formula:
- 15
$$\text{Li}_x\text{M}_y\text{V}_z\text{O}_{8-\delta}\text{F}_\delta$$
- wherein:
- (i) $0 < \delta \leq 1$;
 - (ii) $0 \leq y \leq 0.5$;
 - (iii) x is non-zero;
 - 20 (iv) x, y and z are selected such that the average oxidation state of V is at least 4.6; and
 - (v) M is selected from Al, Si, P, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, La and mixtures thereof.

17. A method of modifying a nominal vanadium oxide formulation of $\text{Li}_x\text{V}_3\text{O}_8$, wherein $1 \leq x \leq 1.5$, for use as an electrode material; said method comprising a step of:

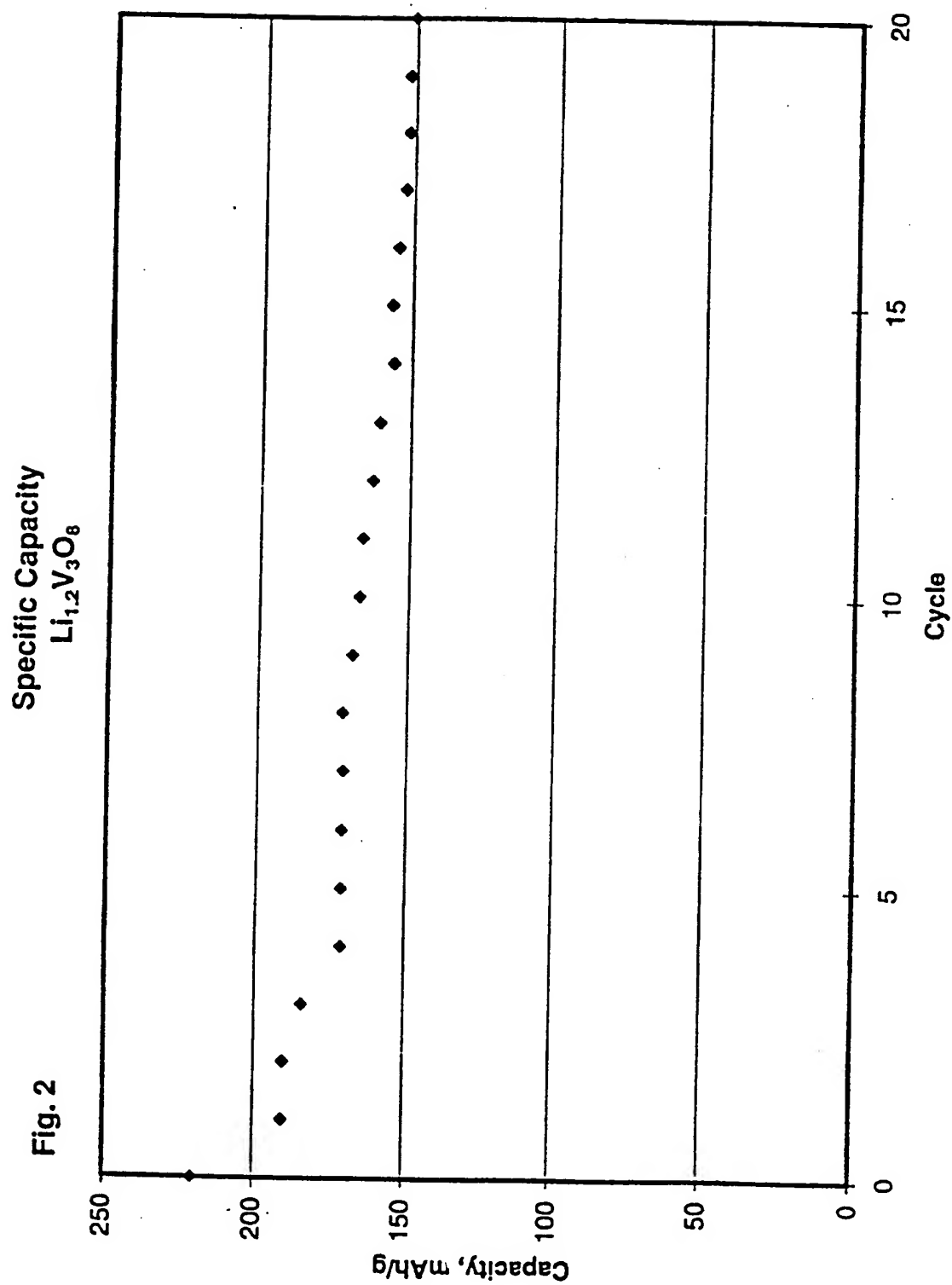
- 5 (a) providing fluorine-doping of the formulation to form a fluorine-doped base formulation, having an average vanadium oxidation state of at least 4.6.

18. A method according to claim 17 further including a step of:

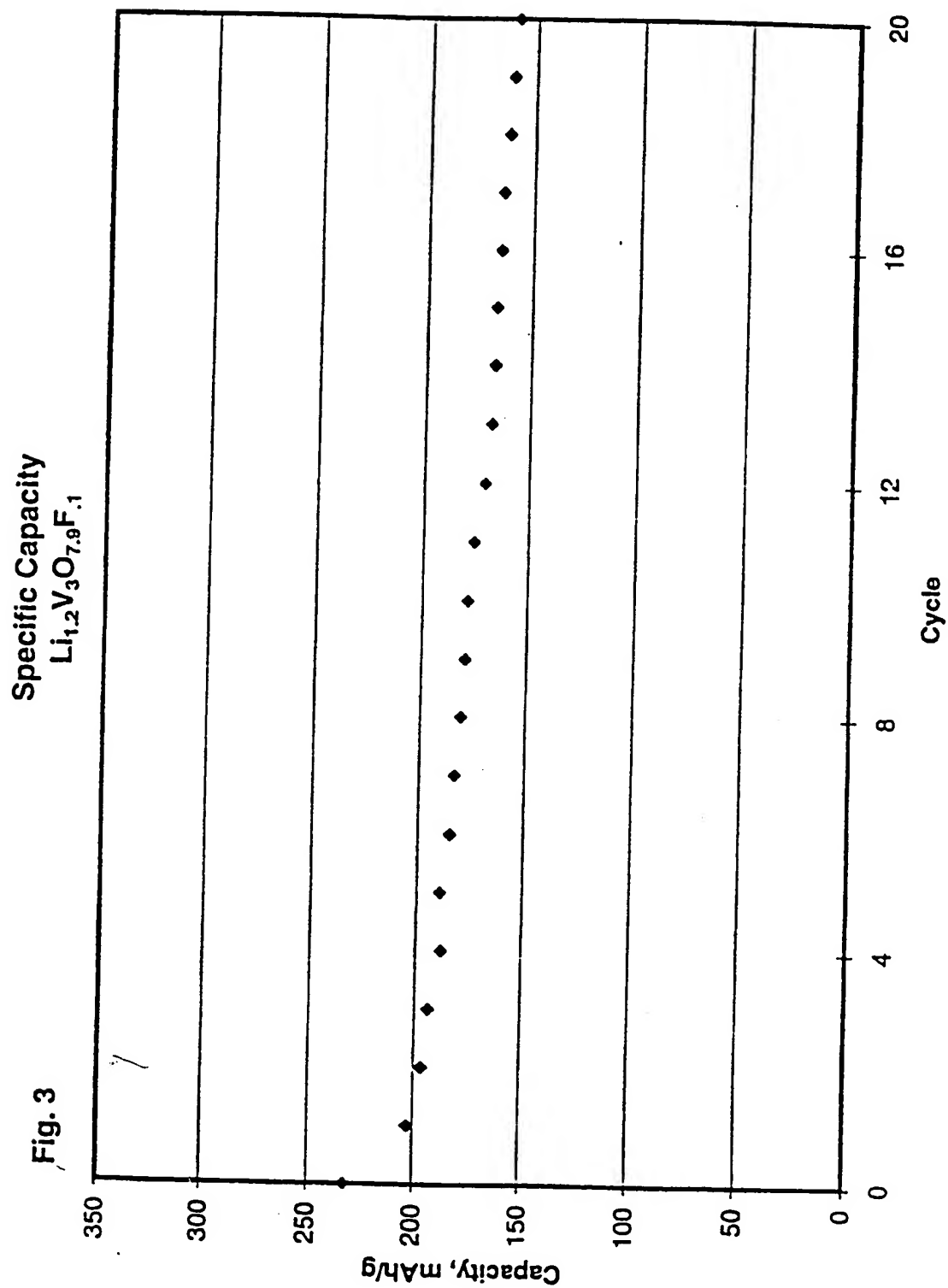
- 10 (a) also doping with cation M selected from the group Al, Si, P, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, La and mixtures thereof.



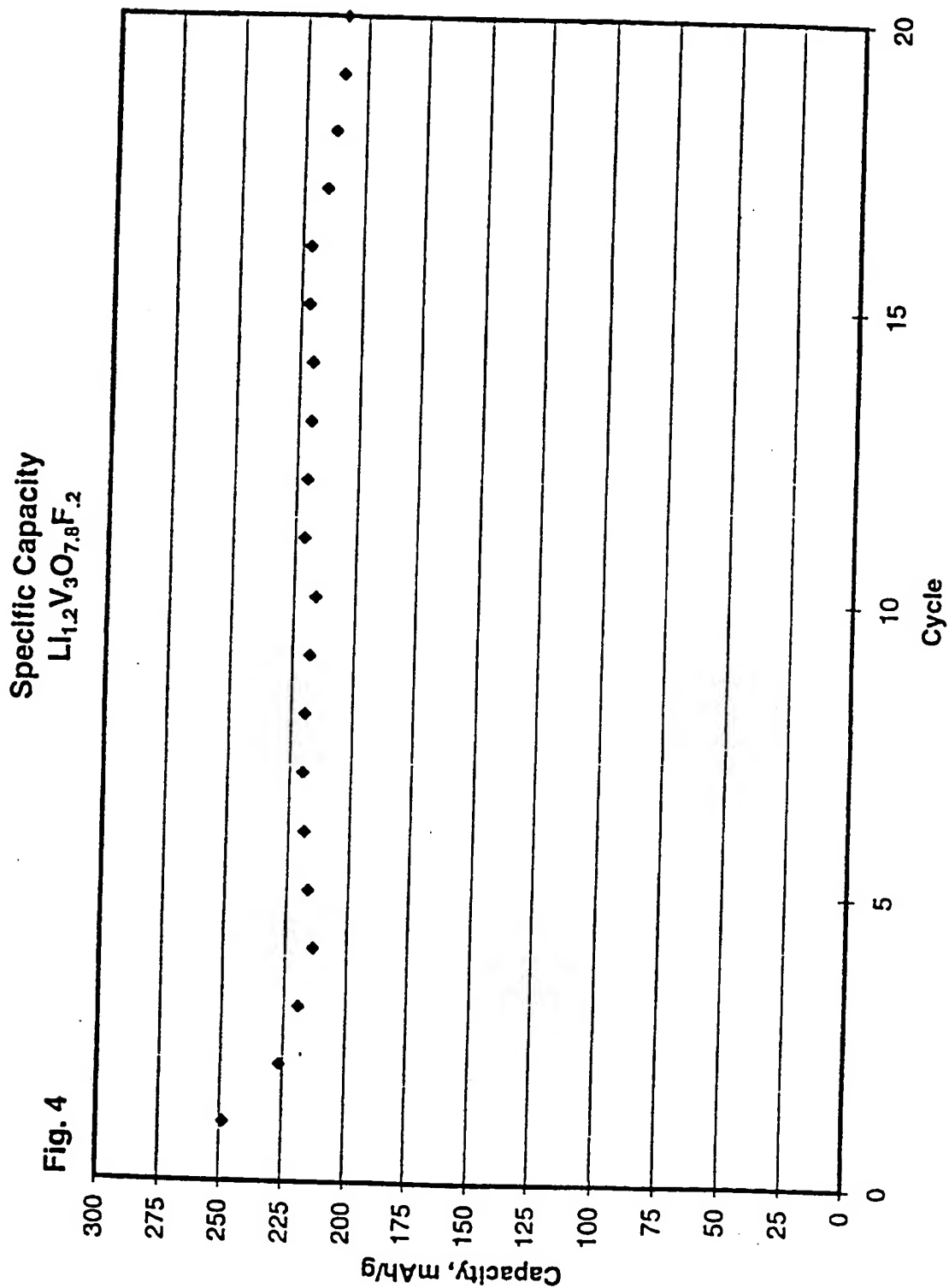
2/18



3/18

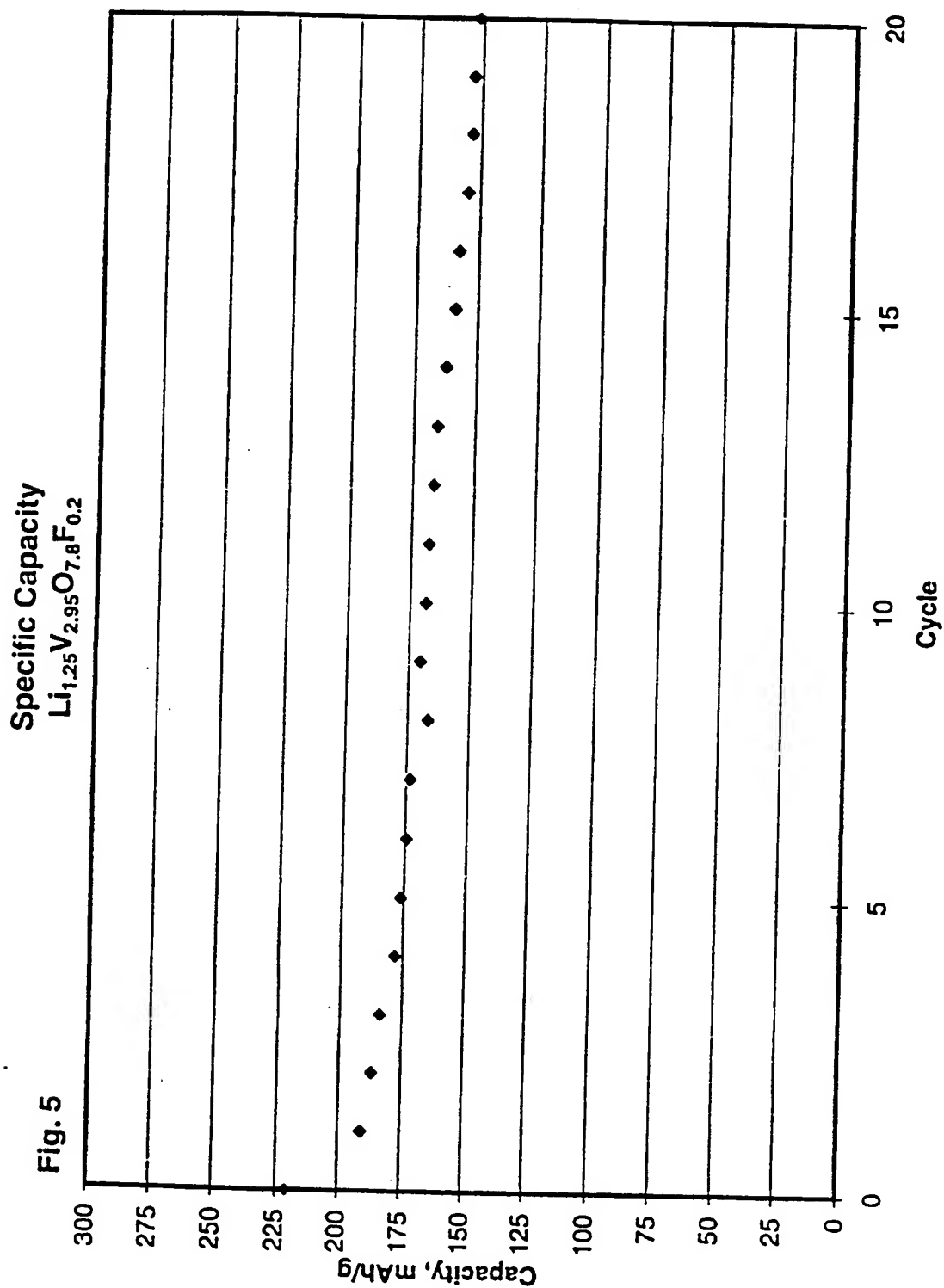


4/18

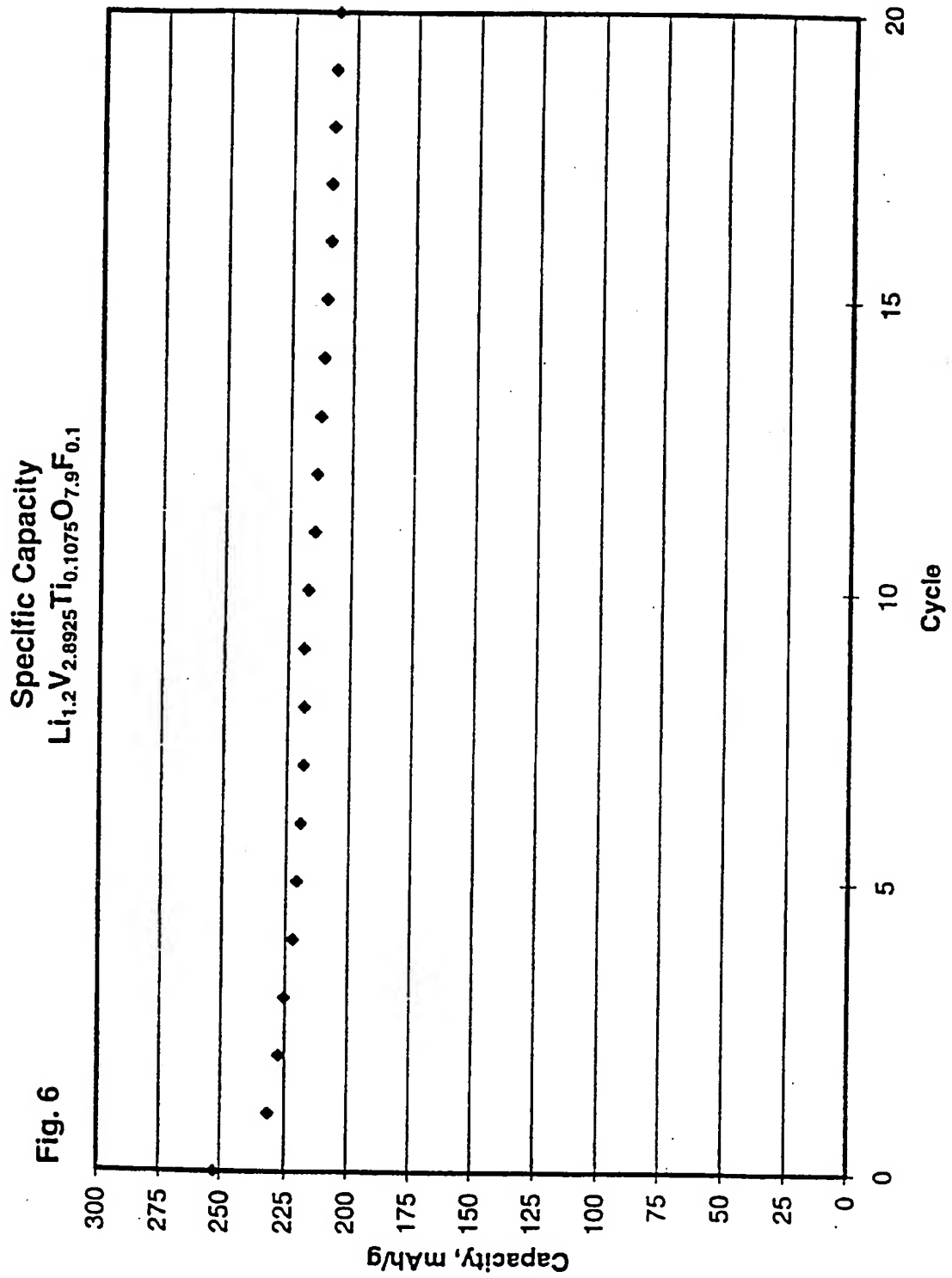


Es333

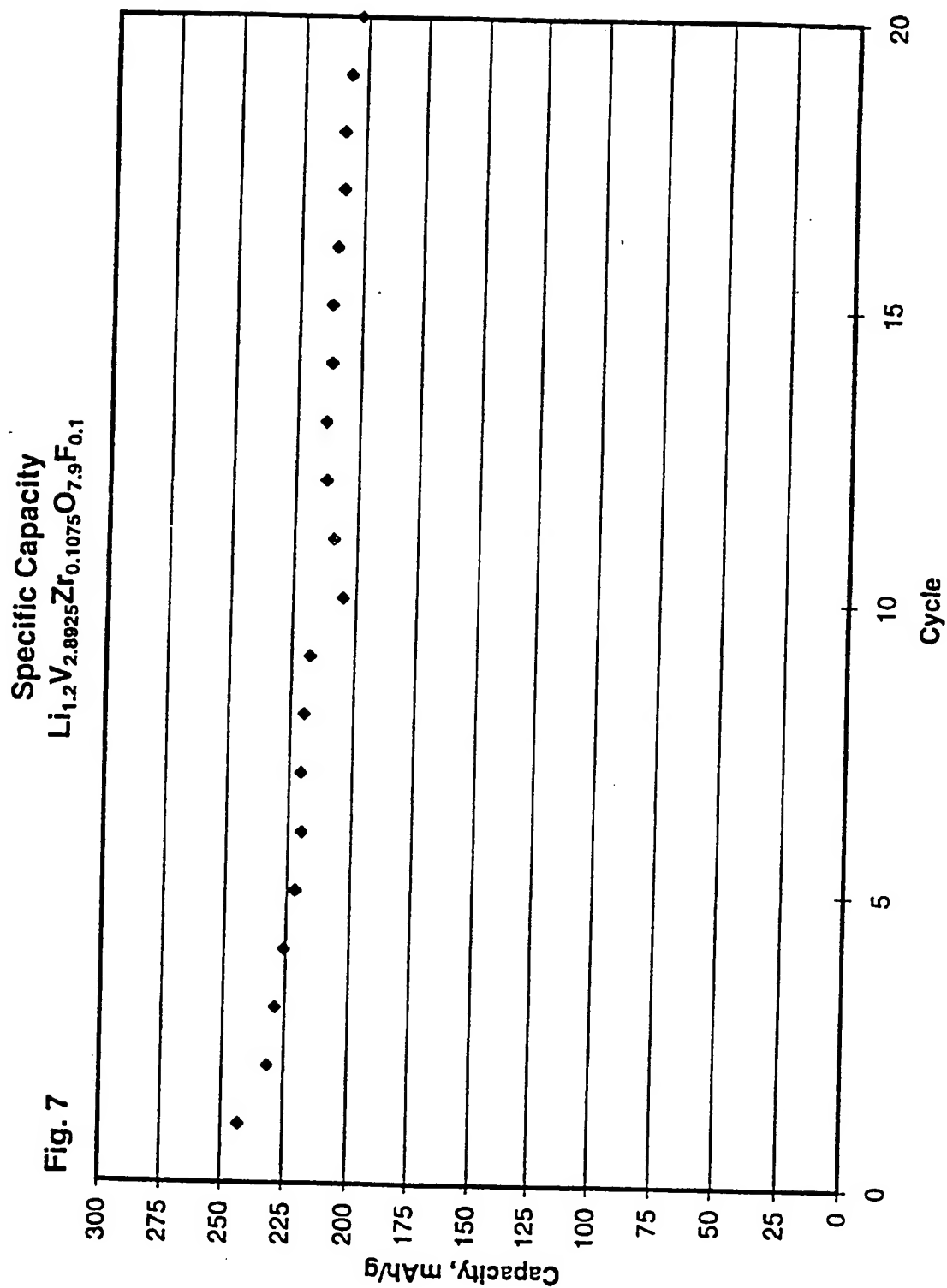
5/18



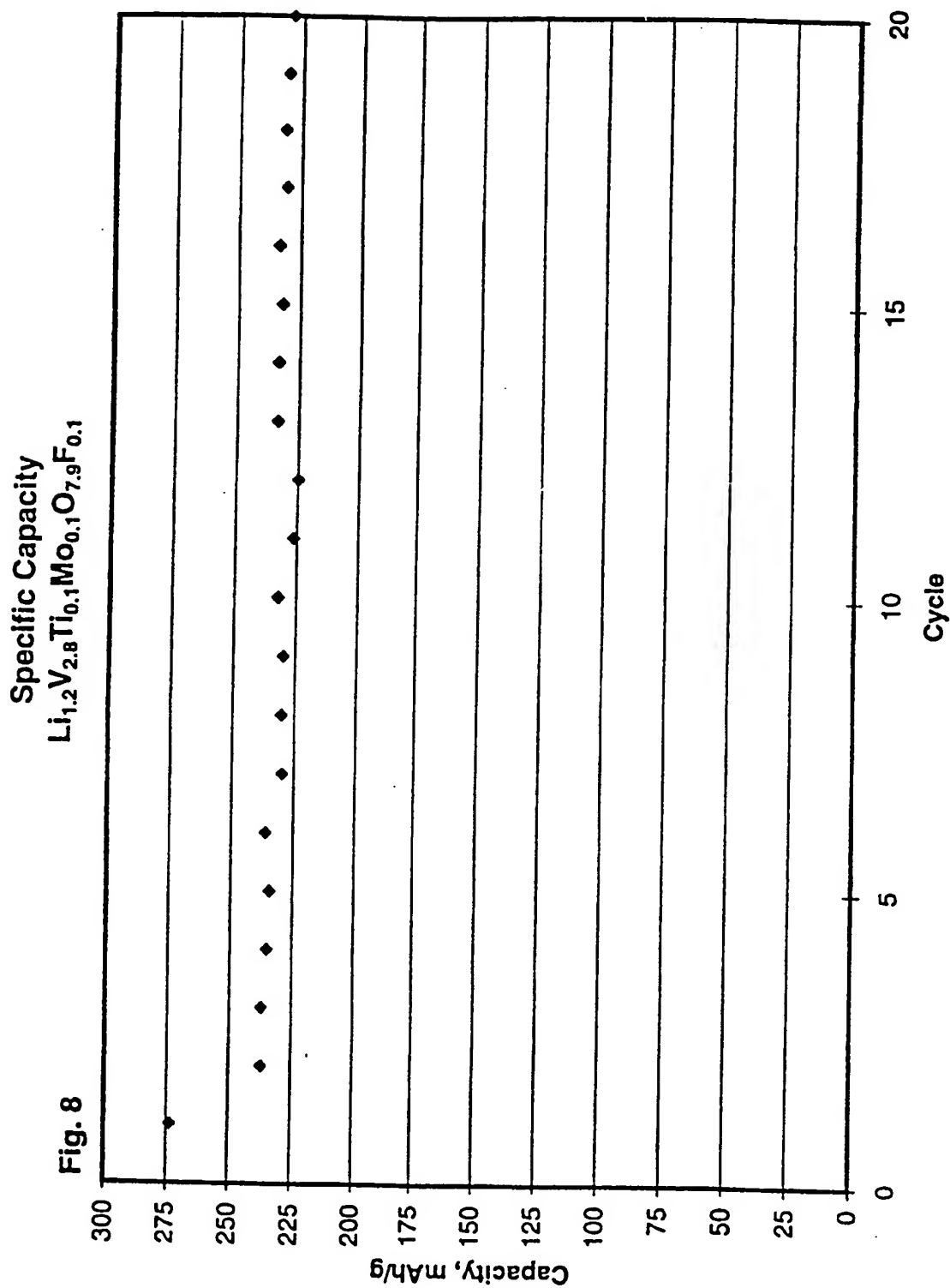
6/18



7/18



8/18



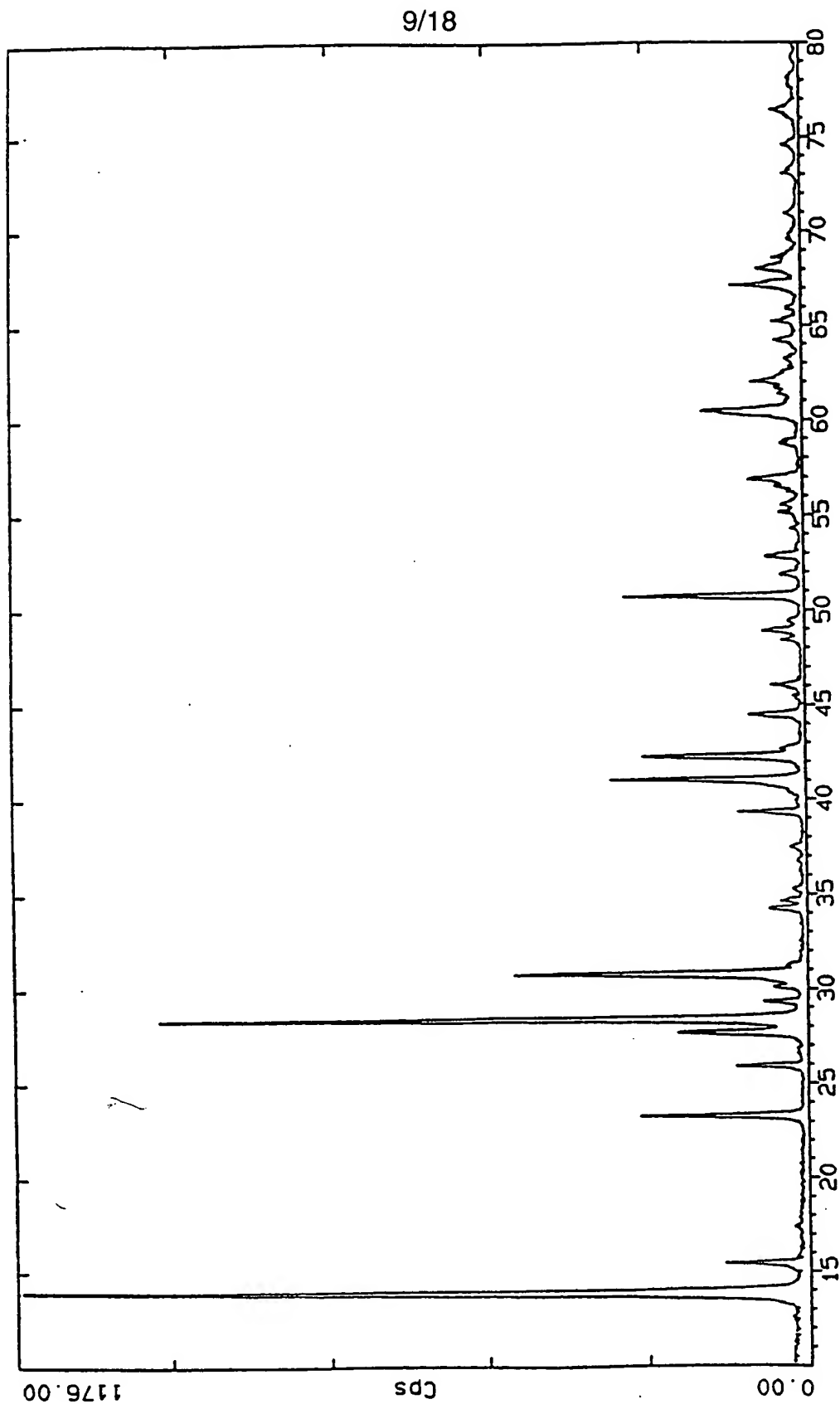


FIG. 9

10/18

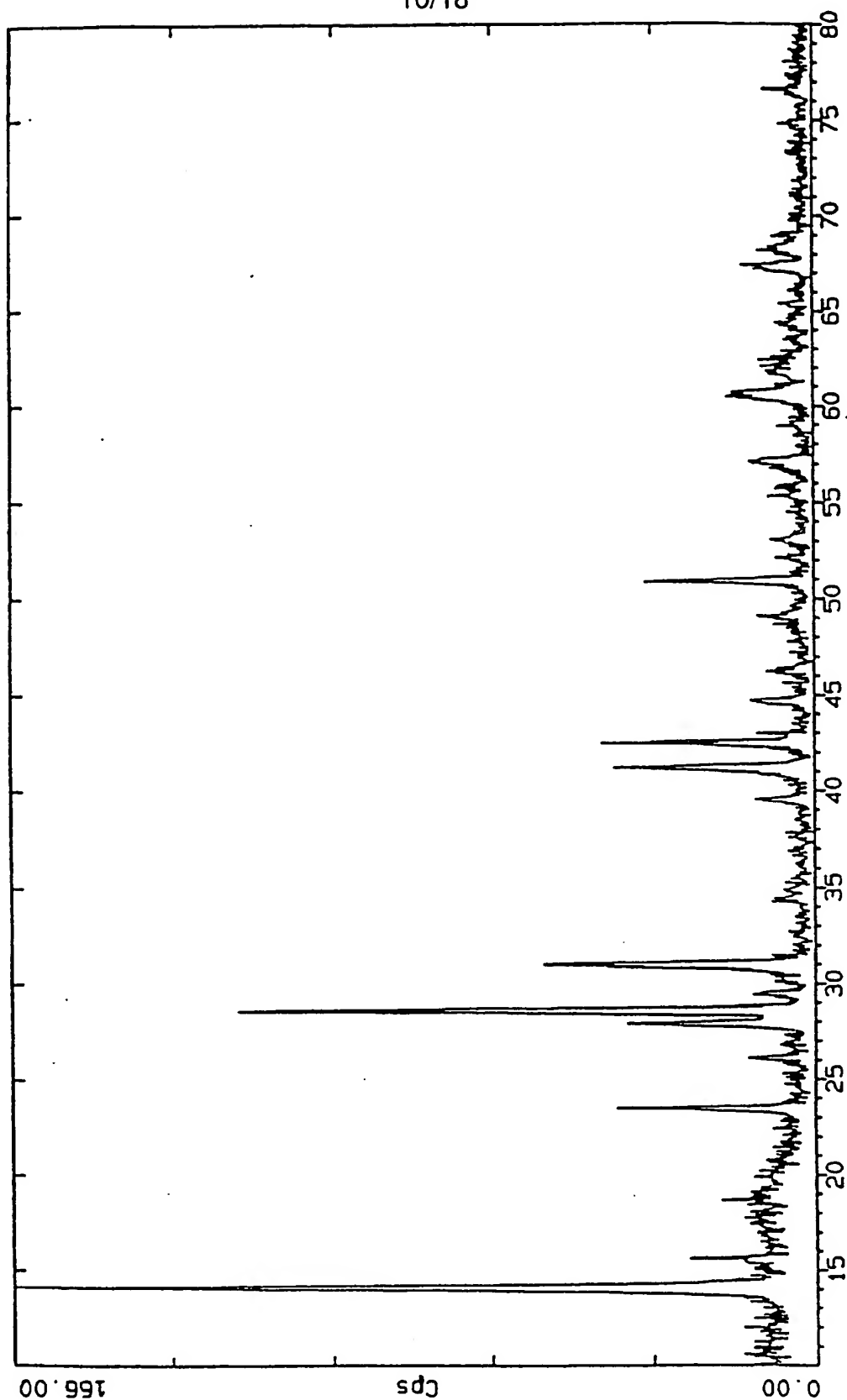


FIG. 10

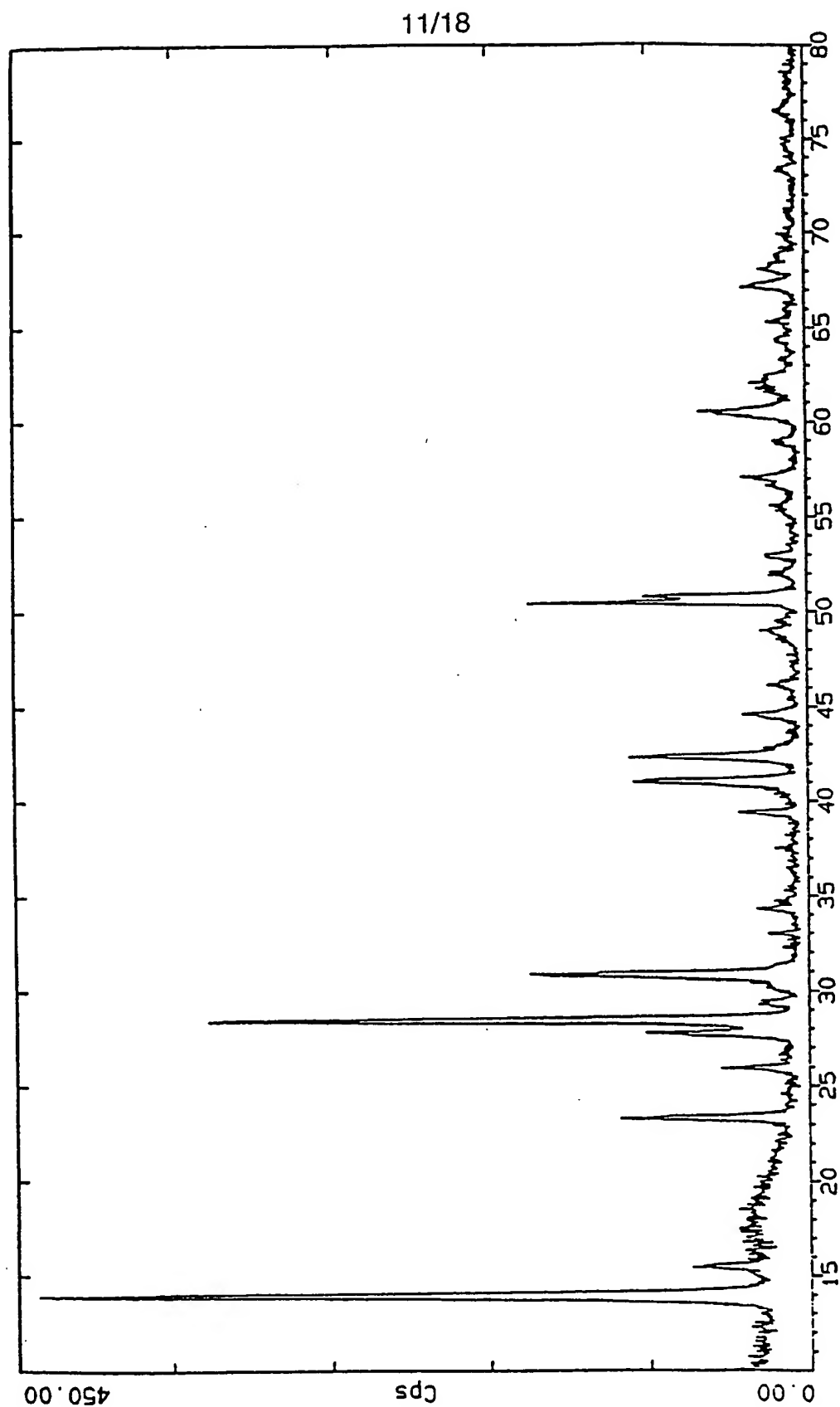


FIG. 11

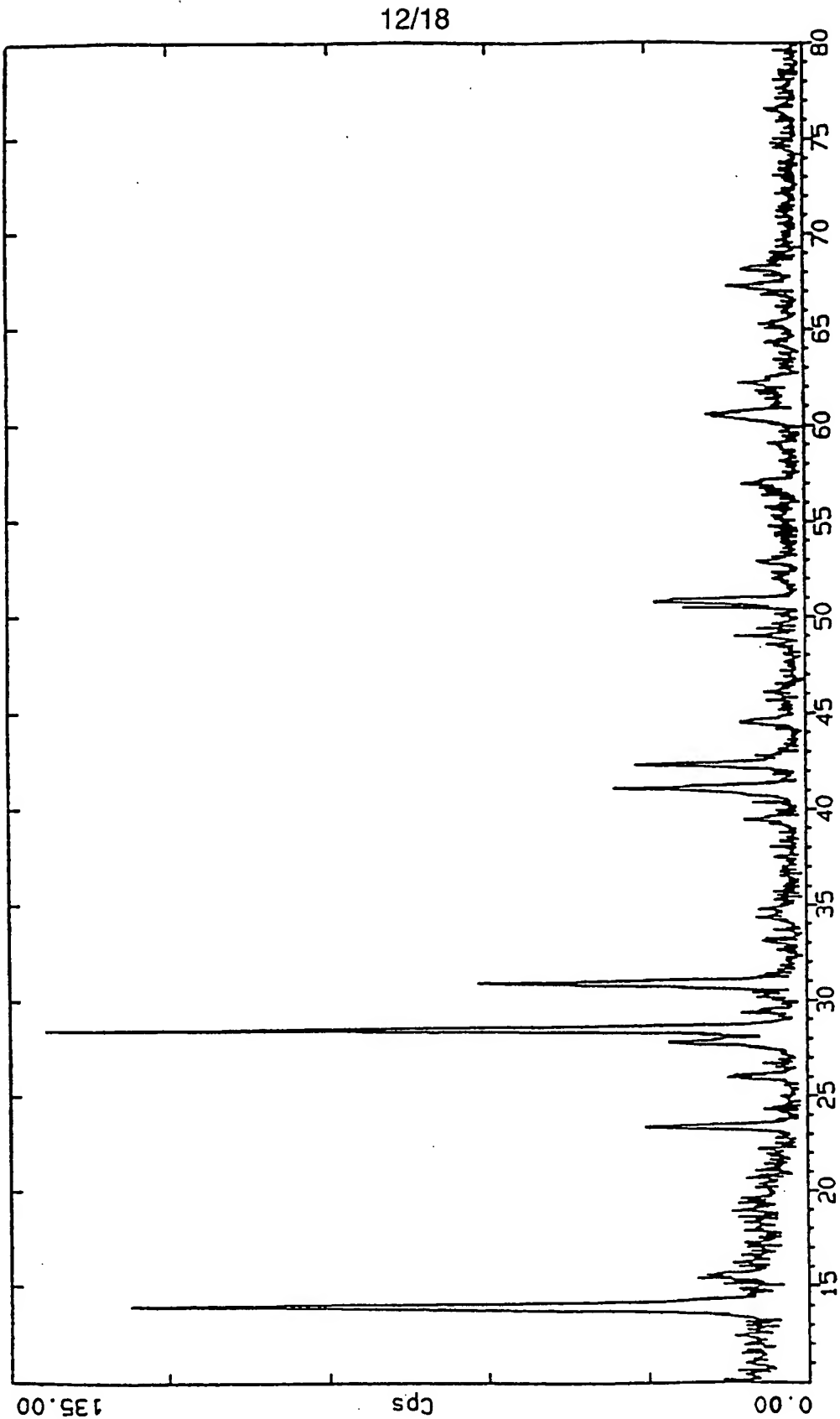


FIG. 12

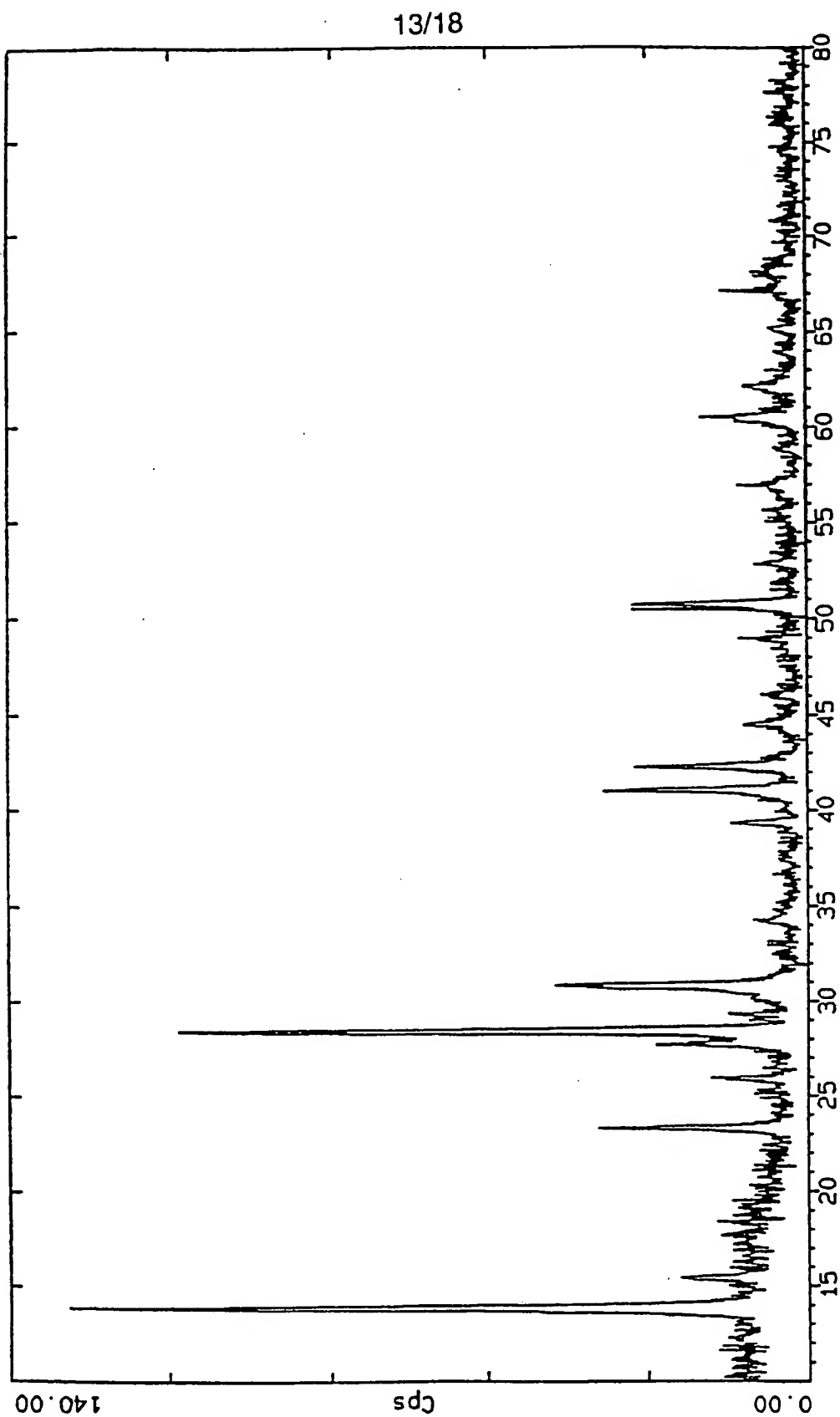


FIG. 13

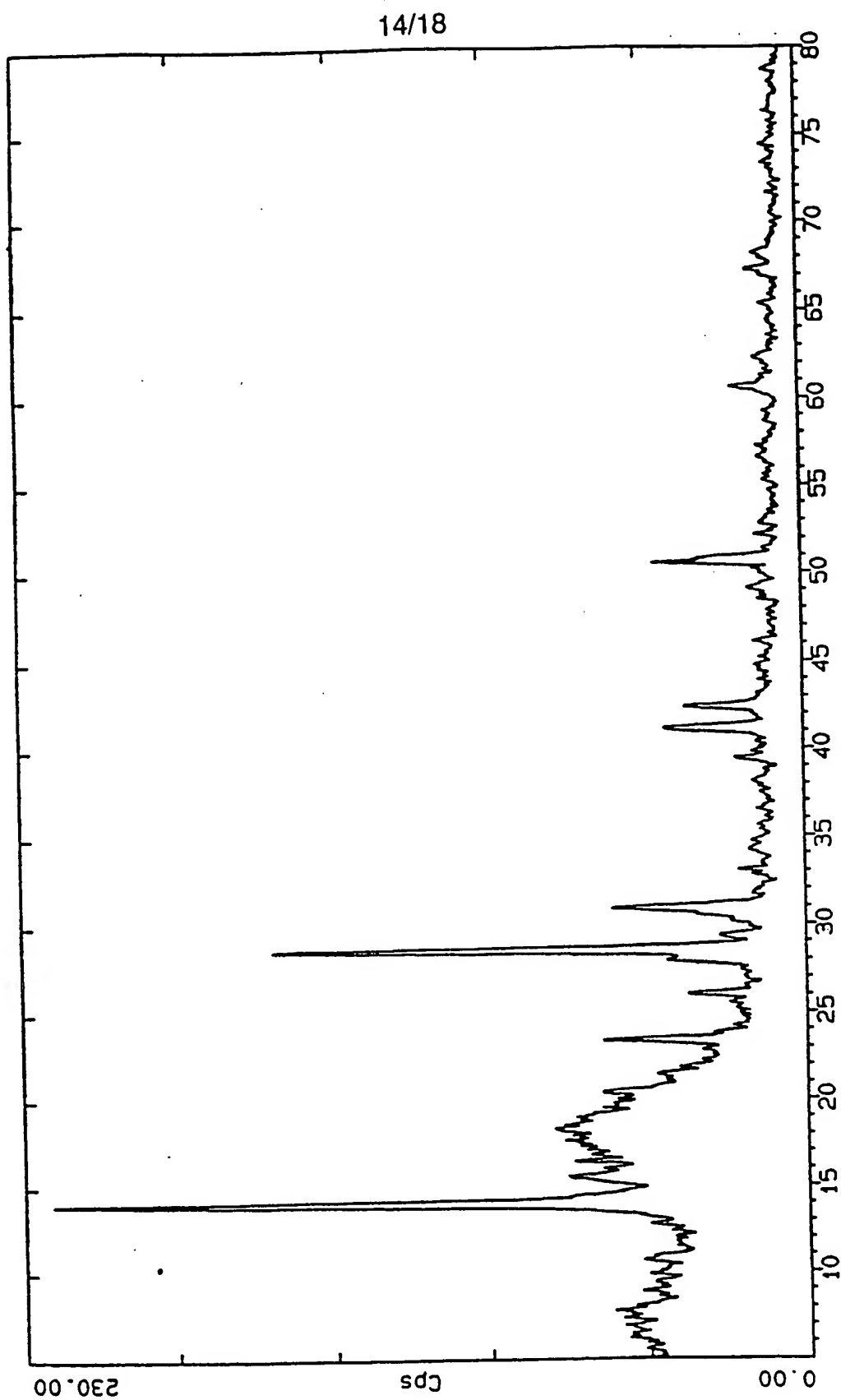


FIG. 14

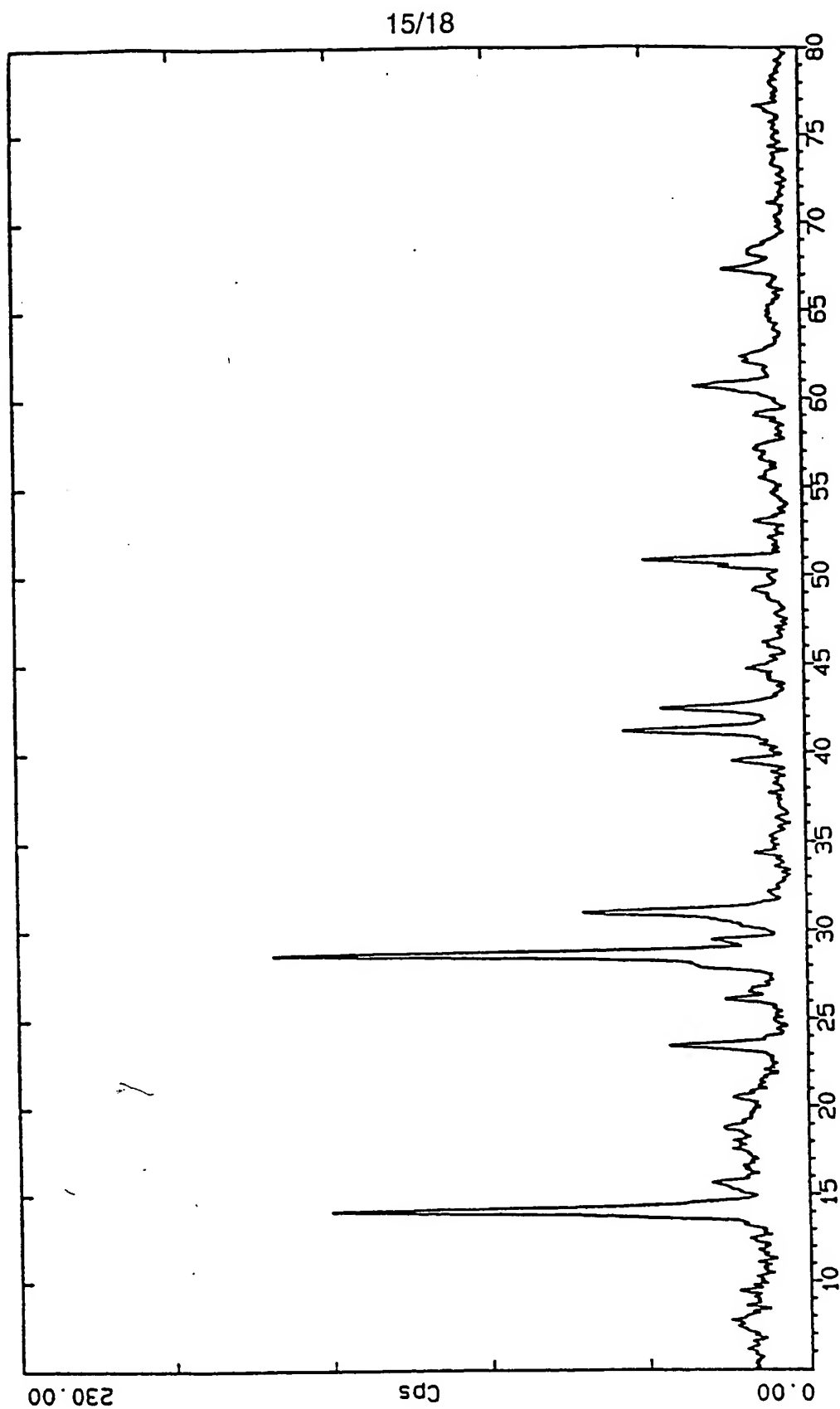


FIG. 15

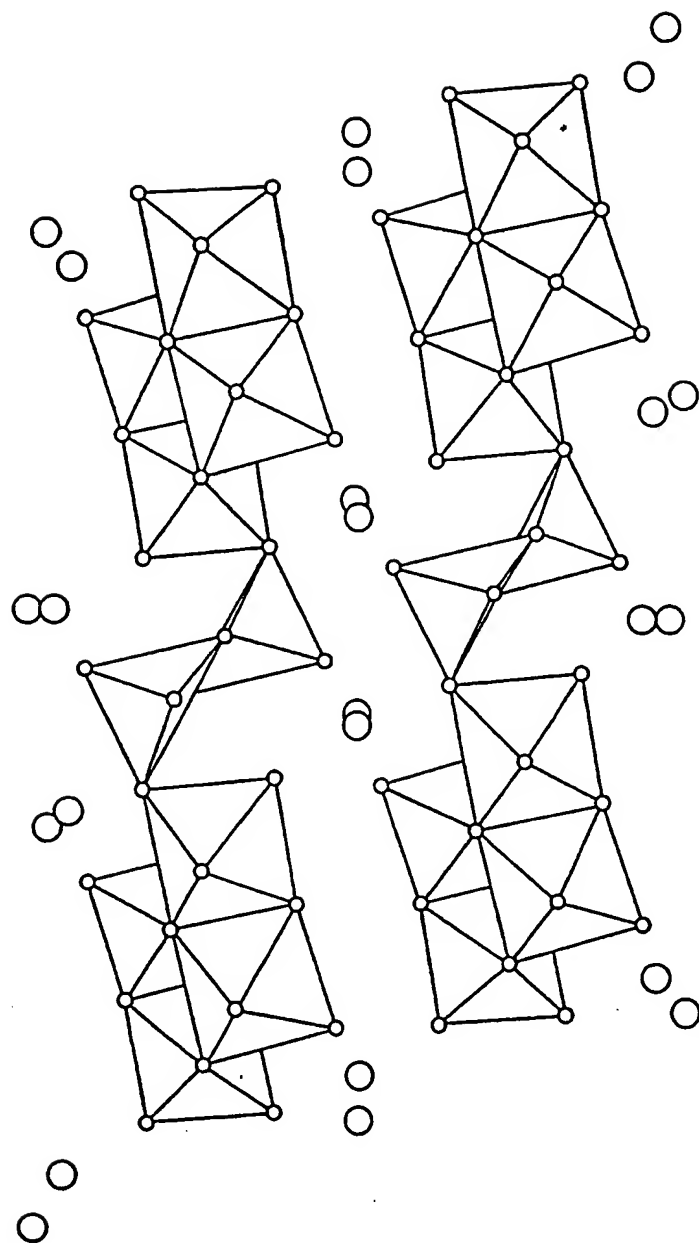


FIG.16

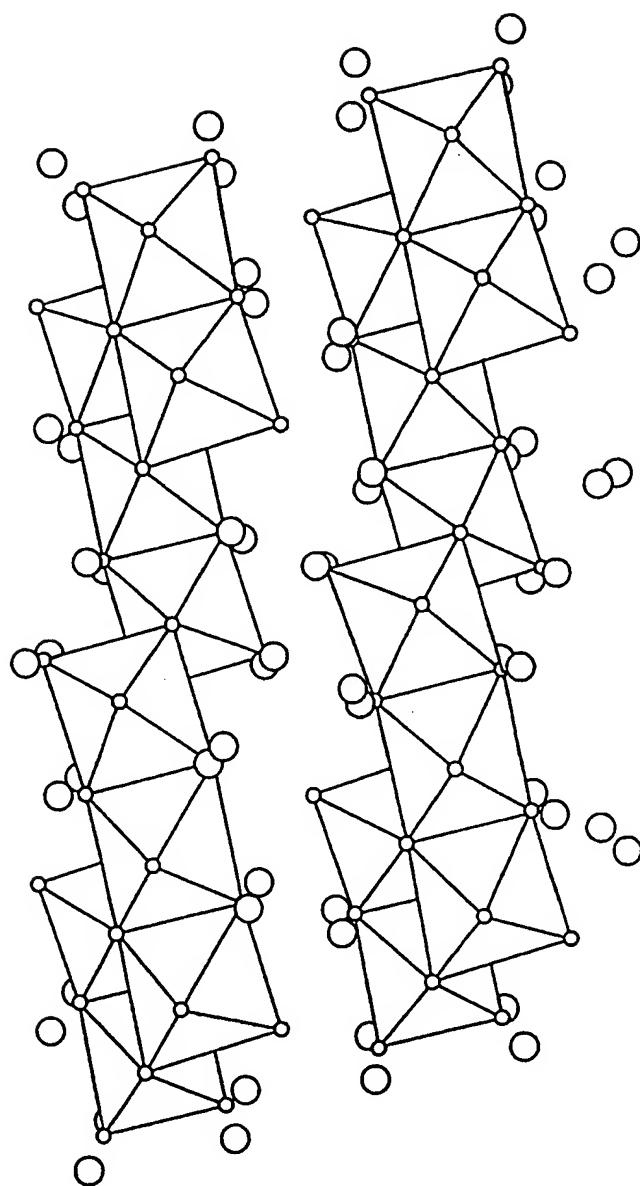


FIG.17

18/18

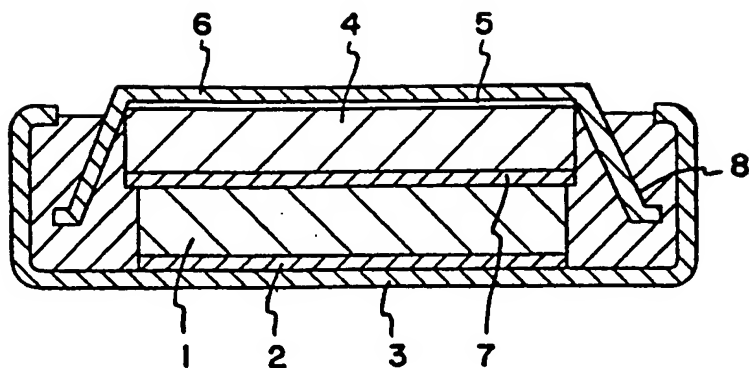


FIG. 18

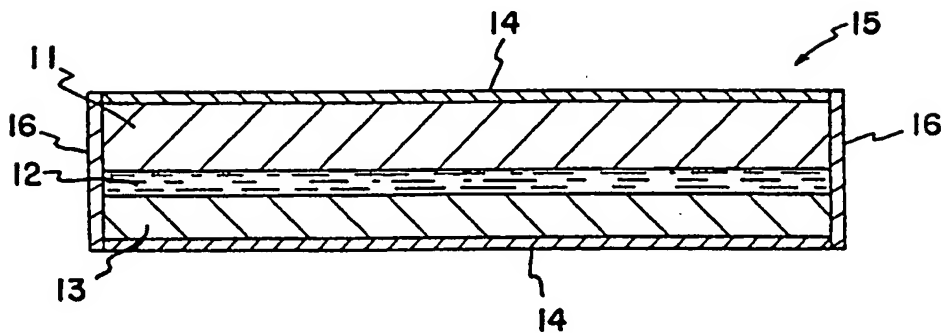


FIG. 19

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 98/25613

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01M 4/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: H01M, C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0394917 A1 (BRIDGESTONE CORPORATION), 31 October 1990 (31.10.90), page 2, line 1 - line 41 --	
A	EP 0397608 A2 (CONSIGLIO NAZIONALE DELLE RICERCHE), 14 November 1990 (14.11.90), column 1, line 38 - column 2, line 20 --	
A	US 5674645 A (GLENN G. AMATUCCI ET AL), 7 October 1997 (07.10.97), column 1, line 60 - column 2, line 30 -- -----	

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z document member of the same patent family

Date of the actual completion of the international search

12 April 1999

Date of mailing of the international search report

18 05 99

Name and mailing address of the ISA,
European Patent Office, P.O. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

ULLA GRANLUND

SA .7379

INTERNATIONAL SEARCH REPORT
Information on patent family membersInternational application No.
PCT/US 98/25613

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
EP	0394917	A1	31/10/90	JP	2288068 A	28/11/90
				US	5013620 A	07/05/91

EP	0397608	A2	14/11/90	AT	108950 T	15/08/94
				CA	2014438 A	12/10/90
				DE	69010763 D,T	09/03/95
				ES	2060999 T	01/12/94
				US	5039582 A	13/08/91

US	5674645	A	07/10/97	NONE		
